Path integral formulation of dissipative quantum dynamics

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Referat

In dieser Dissertation wird der Pfadintegralformalismus auf die Berechnung der Dynamik in dissipativen Quantensystemen angewandt. Behandelt wird die Zeitentwicklung eines Systems von bilinear gekoppelten bosonischen Moden, wobei der Pfadintegralformalismus in kohärenten Zuständen benutzt wird. Diese Methode wird auf einen gedämpften harmonischen Oszillator innerhalb des Caldeira-Leggett-Modells angewandt. Um die stationären Pfade zu bekommen, wurde die Lagrange-Funktion diagonalisiert und anschließend wurde das Pfadintegral mittels der Methode der stationären Phase ausgewertet. Für schwache Systembadkoppelung kann die Zeitentwicklung der reduzierten Dichtematrix in der Basis von kohärenten Zuständenkann in einer einfachen analytischen Form angegeben werden, d.h. in der sogenannten Drehwellen-Näherung kann die Dynamik analytisch ausgewertet werden. Die Terme jenseits der Drehwellen-Näherung konnten nur störunsgtheoretisch behandelt werden. Der Gültigkeitsbereich der Drehwellen-Näherung wird in der Dissertation vom Gesichtspunkt der Spektralgleichungen besprochen. Außerdem wird gezeigt, dass Systeme ohne anfängliche Korrelationen zwischen System und Bad bei kurzen Zeiten Sprünge in der Populationdynamik sogar für ziemlich schwache Koppelung besitzen können. Nur mit anfänglichen Korrelationen kann man die klassischen Pfade für die System-Koordinate erhalten.

Auf das Problem von zwei gekoppelten Flächen wird der Pfadintegralformalismus in einer kombinierten Darstellung aus Phasen-Raum und kohärenten Zuständen angewandt. Das System von Interesse wird durch zwei gekoppelten eindimensionale harmonische Potenzialenergieflächen beschrieben, die mit einem Wärmebad verbunden sind. Die Abbildungsmethode wurde verwendet, um die Lagrange-Funktion des elektronischen Teils des Systems umzuschreiben. Durch Verwenden der Influenzfunktional-Methode von Feynman und Vernon konnte das Bades eliminiert werden. Der nicht-Gaußsche Teil des Pfadintegrals wurde dagegen in einer Störungstheorie in der kleinen Koordinatenverschiebung zwischen den Potenzialenergieflächen ausgewertet. Die Schwingungs- und Populationsdynamik werden in der niedrigsten Ordnung der Störung betrachtet und die Dynamik eines Gaußschen Wellenpakets wird entlang einer eindimensionalen Reaktionskoordinate analysiert. Auch die Dämpfungsrate der Kohärenz im elektronischen Teil des relevanten Systems wird innerhalb der üblichen und der Variationsstörungstheorie ausgewertet. Die analytischen Ausdrücke für die Ratenfunktionen wurden in den Bereichen niedriger und hoher Temperatur berechnet.

Schlagwörter

Dissipative Quantendynamik, Pfadintegrale, kohärente Zustände, reduzierte Dichtematrix, Dissipation, Influenzfunktional, dissipativer harmonischer Oszillator, Elektronen-

transfer, Variationsstörungstheorie

Contents

Chapter 1

Introduction

The behaviour of open quantum systems has attracted more and more interest in the last three decades. The dissipation in a quantum system caused by the interaction of a system with its environment leads to interesting physical phenomena. Two very important examples of quantum dissipative systems are the quantum Brownian motion and the electron transfer process. The latter one plays an exceptionally important role in physics and chemistry (charge transfer in condensed media, chemical reactions in solutions, photosynthetic reactions, etc.) [4, 6].

Besides, the dissipation is accompanied by the decoherence in quantum systems which plays the key role in the processes of quantum measurements [66–68]. In principle, real quantum systems are never isolated from their surrounding environment, in particular, in the process of a measurement. Thus, the non-observability of a quantum superposition is caused by the decoherence in a system, and in this process of decoherence the quantum object is driven from the initial superposition of states to a statistical mixture of them. This evolution of a system can be described by the method of restricted path integrals [64, 65]. Furthermore, the influence of the environment on the system is responsible for the selection of the observable states [71].

The problem of describing damping in open quantum systems has been discussed for a long time in the literature (see, for example, [103]). Among the first treatments of such problems were the quantization of the classical equation of motion like the Langevin equation for a Brownian particle. The most general approach to model quantum dissipation is based on the system-plus-bath model, i.e. the whole system is split into a relevant system consisting of a few degrees of freedom and a thermal bath represented by a large or infinite number of degrees of freedom. The main treatment for the theoretical investigation of such systems is the reduced density matrix formalism. Within this method one starts from the equation of motion for the density matrix of the whole system and then, eliminating the environmental degrees of freedom, one obtains the equation describing the time evolution of the relevant system only.

Actually, most of the calculations present different kinds of perturbation theories. One of the well-known methods is the Redfield theory based on a master equation which treats the system-bath coupling perturbatively and is restricted to the Markov approximation [7, 60, 76]. Often further approximations are performed in addition to the Redfield theory such as the secular approximation [60] or, for the electron transfer processes, the perturbative treatment in the intercenter coupling [26,44]. In Ref. [20] the authors derived a non-equilibrium golden rule formula for the electronic population in the case of strong system-bath coupling but weak intercenter one. Recent exact numerical treatments include multilevel blocking Monte Carlo simulations [70], a formulation of the reduced density matrix in terms of stochastic Schrödinger equations [90] and the self-consistent hybrid approach [96, 102] in which the boundary between relevant system and classically treated bath is varied systematically. The stochastic interpretation of the influence of a thermal bath was recently applied to some model systems [23,91,92]. The implementation of the latter methodology using the stochastic decoupling of the system-bath interaction was performed for the spin-boson system in Ref. [85, 108].

A more general method without the restriction to weak damping is the Feynman-Vernon path integral approach [30, 31] which uses the functional integral technique in a phase-space representation and treats the bath explicitly. This approach allows one to investigate the quantum dynamics of dissipative systems with arbitrarily strong friction and has been successfully applied (see, for example, [34, 35, 52, 53, 56]). Within this path integral formulation the bath can be eliminated exactly, and the problem is reduced to the calculation of the path integral for a relevant system. Further calculations of the remaining path integrals can be performed by means of a perturbation theory in some system parameter if the integral is non-Gaussian. One type of these perturbative treatments was applied to the description of the electron transfer process with small intercenter coupling [55]. Another way of evaluating the system path integral for the two-level system is the non-interacting blip approximation [52] which is a powerful tool for the calculation of the dynamics of spin-boson systems [17, 51, 80]. The validity range of the non-interacting blip approximation has been investigated in Ref. [21] by comparison to some exact methods. Numerical methods for calculating the path integrals for dissipative dynamics were developed in Refs. [56, 88, 97]. The numerical approaches are based on a decomposition of the path integral into a series of short time propagators.

The investigation of the nuclear dynamics in molecules plays an important role in, for example, chemical reaction dynamics. These reactions usually occur in the condensed phase where the reaction coordinate describing the nuclear motion is coupled to the environment. The initial state of the reaction coordinate can be prepared as a wave-packet, i.e. coherent superposition of the vibrational eigenstates by the ultrashort laser pulses. The experimental realization of this preparation is described in Refs. [5,109]. The observation of the dissipative vibrational dynamics of the relevant vibrational mode is accessible in pump-probe experiments.

The present work is devoted to the development of some analytic approximate methods for the calculation of the dissipative dynamics in quantum systems which are based on the path integral formulation of the reduced density matrix. We investigated the dynamics of two model systems: the quantum damped harmonic oscillator and the two level system with vibrational sublevels (curve-crossing system). In both cases the dissipative dynamics of the relevant vibrational coordinate has been analyzed.

This thesis is organized as follows: Chapter 2 gives a brief introduction to the models of dissipation and the mathematical methods of calculating the reduced dynamics. We discuss the system-plus-bath models and, in particular, the well-known model of Caldeira and Leggett [12–14]. Then the description of the procedure of eliminating the bath based on the master equation and the path integral formulation is given. In the last section we concentrate on the Feynman-Vernon influence functional approach which will be used in the next chapters of this thesis.

In chapter 3 we develop the real-time path integral technique and derive the forward and backward coherent state path integrals. Then this formulation is applied to a quantum damped harmonic oscillator within the Caldeira-Leggett model. Instead of eliminating the bath within the influence functional approach [34] we diagonalized the Lagrangian function of the system. In this way we obtained a simple expression for the evolution of the relevant system in the presence and in the absence of initial system-bath correlations. Besides, we described the process of decoherence in the system with the help of the Green's function of the system.

A dissipative curve-crossing system is the general model of an electron transfer process. The dynamics of such a system is studied in chapters 4 and 5. The full system is represented by a damped harmonic oscillator within the Caldeira-Leggett model coupled to an electronic two-level system. The density matrix of the whole system is formulated in terms of a combined coherent-state and phase-space path integral and the bath is eliminated exactly by using the influence functional method. We constructed a perturbation theory in the interaction between the electronic subsystem and the dissipative vibrational mode which is valid for a system with small coordinate shift between potential surfaces of each electronic state. This is the case of the electron transfer in the so-called Marcus inverted region which can be met in the intramolecular transfer in organic radical ions [18] and in betain-30 [100]. The results of our perturbative treatment are compared with the results of the Redfield theory in case of small dissipation in order to investigate the validity range of the perturbative approach. In chapter 4 the vibrational dynamics of the reaction coordinate is calculated to the first perturbative order while in chapter 5 we study the dissipative population dynamics of the electronic levels which is of the second perturbative order. We obtained the perturbative expansion for the decoherence rate in the two-level electronic subsystem which then is treated by means of the variational perturbation theory [45, 47]. This method converts divergent weak-coupling expansions into convergent strong coupling expansions.

The main results of the present work are summarized in the last chapter. The Planck constant $\hbar$ and the Boltzmann constant k_b are set to unity throughout this thesis.

Chapter 2

Systems with dissipation: models and methods of calculation

2.1 Classical and quantum description of dissipation

The most simple and important example of a dissipative system is the Brownian motion in a viscous medium. The classical motion of a Brownian particle with mass M and coordinate x moving in the potential $V(x,t)$ can be described by the Langevin equation

$$M\ddot{x}(t) + 2M\int_0^t ds\gamma(t-s)\dot{x}(s) + \frac{\partial V(x,t)}{\partial x} = \mathcal{F}(t) \ , \qquad \langle \mathcal{F}(t)\rangle = 0 \ , \tag{2.1}$$

where $\mathcal{F}$ is a Gaussian fluctuating force acting on the particle and $\gamma(s)$ describes the friction. The statistical properties of the function $\mathcal{F}$ are characterized by the time-correlation function $\langle \mathcal{F}(t)\mathcal{F}(t')\rangle$ which is determined by the environment. But at low temperatures of the environment quantum effects in the behaviour of the particle become important. One of the first ways of constructing a quantum theory of dissipation was the quantization of the classical equations of motion. However, a classical dissipative equation like the Langevin equation contradicts the uncertainty relation which must be satisfied in the quantum theory [54]. Another problem with the quantization of the classical equation is connected to the irreversibility of the dynamics described by this equation. The quantum description of dissipation must start from a reversible dynamics described by some Hermitian Hamiltonian and then one gets the irreversibility after some additional assumptions. But the irreversibility in the Langevin equation is introduced from the beginning. In contrast to the phenomenological way, the quantum Langevin equation can be obtained from the forward-backward path integrals within some concrete quantum model of dissipation (see, for example, [45]).

The physical cause of dissipation is the influence of the environment on the relevant system. Hence a consecutive quantum theory of dissipative systems should be derived using some dissipative Hamiltonian in which the surrounding medium and its influence on the system are taken into account. This leads to the so-called system-plus-bath model where the full system is split into the relevant system consisting of a few degrees of freedom and a thermal bath represented by a large or infinite number of degrees of freedom. The

Hamiltonian of this model is given in the form

$$H = H_s + H_b + H_i \tag{2.2}$$

where H_s and H_b describe the relevant system and the bath, respectively, and the term H_i represents the interaction between the system and the bath which leads to the dissipation in the system. This description of the dissipation depends on the concrete model of the bath and on the form of the system-bath interaction which will be considered in the next section.

2.2 Caldeira-Leggett model

The most famous model of the bath and the system-bath interaction is the Caldeira-Leggett model [12–14] which was constructed in order to describe the diffusion of the quantum particle moving in a dissipative medium. This model is of the system-plus-bath type and the Hamiltonian of this model reads

$$H_{CL} = H_s + H_b + H_i + H_r \tag{2.3}$$

where the system is one particle moving in the potential V

$$H_s = \frac{p^2}{2M} + V(x) \ . \tag{2.4}$$

The medium is supposed to consist of a large number of atoms interacting with each other and oscillating around their equilibrium states with small deviations. Performing the normal mode transformation one can describe the bath by a number of independent harmonic oscillators

$$H_b = \sum_\omega \left(\frac{p_\omega^2}{2m_\omega} + \frac{m_\omega \omega^2 x_\omega^2}{2} \right) \ . \tag{2.5}$$

The interaction between the system and the bath is assumed to be bilinear in the system and bath coordinates

$$H_i = -x \sum_\omega c_\omega x_\omega \ . \tag{2.6}$$

The last term in Eq. (2.3) represents the so-called counterterm which renormalizes the system potential

$$H_r = x^2 \sum_\omega \frac{c_\omega^2}{2m_\omega \omega^2} \ . \tag{2.7}$$

A detailed discussion of the role of the counterterm is given in Chapter 3 for the example of the damped harmonic oscillator. As will be shown below, this form of the system-bath interaction allows us to take into account the influence of the bath on the system exactly using the path integral technique.

Actually, the quantum dynamics of a finite number of degrees of freedom described by the Hamiltonian (2.3) is reversible while the dissipative dynamics is irreversible. The important step is to perform the continuum limit for the bath modes introducing the spectral density function for the bath which contains the information about the bath modes and their interaction with the system:

$$J(\omega') = \frac{\pi}{2} \sum_{\omega} \frac{c_{\omega}^{2}}{m_{\omega}\omega} \delta(\omega - \omega') \ . \tag{2.8}$$

Since the environment is very large in comparison to the relevant system, it is reasonable to assume that the number of degrees of freedom in the bath is infinite, and the spectral density function is a continuous function of the frequency of the bath modes. So the sum over frequencies in the interaction part of the Hamiltonian (2.6) can be replaced by an integral. As will be shown in the next chapter, in this way one gets complex values for the poles of the Green's function describing the relevant system. It leads to irreversibility in the dynamics of the system and, hence, to dissipation.

2.3 Reduced density matrix formalism

The behaviour of the open system within the system-plus-bath model can be described by the density matrix formalism. Since we are interested only in the dynamics of the relevant system we trace out the bath degrees of freedom from the equation of motion for the density matrix. In this way one gets the reduced density matrix

$$\rho_s(t) = \mathrm{Tr}_b \rho(t) \tag{2.9}$$

which gives the time evolution of the system under the influence of an environment. The first method to get the equation of motion for the reduced density matrix (RDM) is to use the von Neumann equation for the full density matrix $\dot{\rho}(t) = -i[H(t), \rho(t)]$ (where H is the Hamiltonian of the full system). The usual assumption is that the whole density operator can be split into a product of operators of the relevant system and the bath $\rho(t) = \rho_s(t) \otimes \rho_b(t)$ where the operators ρ_s and ρ_b act in the vector spaces of the system and the bath, respectively [7]. Additionally, the bath is supposed to be always in the equilibrium state described by the Boltzmann distribution

$$\rho_b = \frac{1}{Z_b} \exp(-H_b/T_b) \ , \tag{2.10}$$

where $Z_b = \mathrm{Tr}_b e^{-H_b/T_b}$ is the bath partition function. The latter condition means that the times of relaxation of the environment are faster than the time scales of the dynamics of the relevant system. In this way one can eliminate the bath and gets a master equation for the reduced density matrix [7, 103]

$$\dot{\rho}_s(t) = -i[H_s, \rho_s(t)] + R\rho_s(t) \tag{2.11}$$

where R is the operator which is responsible for the dissipation. Actually, the theories based on master equations are usually restricted to weak system-bath interaction since one is able to eliminate the bath from the von Neumann equation only with this assumption. The exceptions consist of master equations obtained by the path integral method which allows to eliminate the bath exactly in case of bilinear system-bath coupling [40, 77]. This method of calculation of the RDM based on the master equation was used for various problems like the damped harmonic oscillator [32, 38, 75, 101], electron and exciton transfer [36, 37, 44, 55, 110] and many others. Further approximations like the Markov approximation which consists of neglecting the memory effects lead to the Redfield equation [44, 61, 62, 81].

Another way to calculate the time evolution of the reduced density matrix is the path integral technique based on the equation for the full density matrix in the Heisenberg picture

$$\rho(t) = e^{-iHt}\rho(0)e^{iHt} \ . \tag{2.12}$$

One can write the evolution operators as functional integrals [31] and then eliminate the bath by integrating over the end points of the bath trajectories. It turns out that within the Caldeira-Leggett model of bilinear system-bath coupling the bath can be eliminated exactly using the functional integral treatment. Thus this method is not restricted to the weak system-bath coupling in comparison to most master equations. However, the functional integral over the system trajectories is not mandatorily Gaussian and usually not calculable exactly.

Analytic evaluations of functional integrals are usually restricted to quadratic Hamiltonians (Gaussian integrals), the semiclassical limit or a perturbative treatment in some of the system parameters. Among the latter is the so-called noninteracting-blip approximation [52] which is very good for large ranges of system parameters. In the next sections of this chapter we will concentrate on the path integral formulation of the system in the Caldeira-Leggett model and on the procedure of eliminating the bath.

2.4 Feynman path integral formulation

In this section we will give an introduction to the path integral formulation of the quantum dynamics based on the Feynman path integrals [31]. Let us start from the functional integral representation of the evolution operator determining the time evolution of the wave function of the system described by the Hamiltonian H

$$|\Psi(t)\rangle = e^{-iHt}|\Psi(0)\rangle \ . \tag{2.13}$$

In the coordinate representation the above expression reads

$$\langle x|\Psi(t)\rangle = \int dx' \langle x|e^{-iHt}|x'\rangle\langle x'|\Psi(0)\rangle \ , \tag{2.14}$$

where the completeness relation $\int dx|x\rangle\langle x| = 1$ has been used. For simplicity, we assume that the Hamiltonian H is of the standard form, i.e. it is a sum of the kinetic and the potential energy

$$H = H(p, x, t) = T(p, t) + V(x, t) \ , \quad T(p, t) = \frac{p^2}{2M} \ . \tag{2.15}$$

Using Feynman's procedure of slicing the operator e^{-iHt} into a large number of time evolution operators with small propagation time steps, one can get the matrix element of the evolution operator as a functional integral

$$\langle x|e^{-iHt}|x'\rangle = \int D[x(\tau)] \exp\Big\{iS[x(\tau)]\Big\} \ . \tag{2.16}$$

The symbol $D[x(\tau)]$ denotes the integration over all trajectories $x(\tau)$ with fixed end points $x(0) = x'$, $x(t) = x$, and the phase factor S is the action which can be written as an integral of the Lagrangian function

$$S[x(\tau)] = \int_0^t d\tau \mathcal{L}(\dot{x}(\tau), x(\tau)) \ . \tag{2.17}$$

Here the Lagrangian $\mathcal{L}$ is the Lagrangian of the classical particle moving in the potential V

$$\mathcal{L}(\dot{x}(\tau), x(\tau)) = \frac{M}{2}\dot{x}^2(\tau) - V(x(\tau), \tau) \ . \tag{2.18}$$

The expression of the form (2.16) is frequently called the forward path integral. For the backward path integral, i.e. for the matrix element of the conjugated evolution operator e^{iHt} one can write down a similar

$$\langle x|e^{iHt}|x'\rangle = \int D[x(\tau)] \exp\Big\{ - iS[x(\tau)]\Big\} \ , \tag{2.19}$$

where the action S remains the same but the end points of the trajectories are now $x(0) = x, \ x(t) = x'$.

2.5 Influence functional method

Now we can consider the density matrix of the system described by the Caldeira-Leggett Hamiltonian using the path integral formalism presented in the previous section. Below the procedure of eliminating a bath within the influence functional method [30, 31, 34] is presented. Let us write the forward path integral as the matrix element of the operator of evolution from the initial state $|\{x_{\omega i}\}\rangle|x_i\rangle$ to the final state $|\{x_{\omega f}\}\rangle|x_f\rangle$ (here $|x\rangle$ is the vector of state of the system particle and $|\{x_\omega\}\rangle = \prod_\omega |x_\omega\rangle$ is the vector of states of the bath modes)

$$\langle x_f|\langle\{x_{\omega f}\}|e^{-iHt}|\{x_{\omega i}\}\rangle|x_i\rangle = \int D[x(\tau)]D[\{x_\omega(\tau)\}] \exp\{iS[x, \{x_\omega\}]\} \tag{2.20}$$

where $x(\tau)$ and $x_\omega(\tau)$ denote the trajectories of the system particle and the bath mode with the frequency ω, respectively. The action of the full system reads

$$\begin{aligned} S[x, \{x_\omega\}] = \int_0^t d\tau \Bigg[& \frac{M}{2}\dot{x}^2(\tau) - V(x(\tau)) \\ + \sum_\omega \bigg(& \frac{m_\omega}{2}\dot{x}_\omega^2(\tau) - \frac{m_\omega \omega^2 x_\omega^2(\tau)}{2} + c_\omega x(\tau) x_\omega(\tau) - x^2(\tau)\frac{c_\omega^2}{2m_\omega\omega^2}\bigg)\Bigg] \ . \end{aligned} \tag{2.21}$$

Then, it is possible to determine the time evolution of the density matrix of the full system substituting the expressions for the forward and backward path integrals into Eq. (2.12). At this step we should consider some concrete initial conditions for the full system. Let us assume that the relevant system and the bath were prepared independently, i.e. their initial density matrix is factorized

$$\rho(0) = \rho_s(0)\rho_b(0) \tag{2.22}$$

where ρ_s and ρ_b correspond to the density operators of system and bath, respectively. Besides, it is reasonable to assume that the initial density matrix of the bath is the Boltzmann distribution with some temperature T_b described by Eq. (2.10).

Now our purpose is to get the matrix element of Eq. (2.9). Mathematically this means that we have to eliminate the bath by integration over the bath trajectories $\{x_\omega(\tau)\}$, $\{x'_\omega(\tau)\}$ and their end points

$$\begin{aligned} x_\omega(0) &= x_{\omega i} \ , \qquad & x_\omega(t) &= x_{\omega f} \ , \\ x'_\omega(0) &= x'_{\omega i} \ , \qquad & x'_\omega(t) &= x_{\omega f} \end{aligned} \tag{2.23}$$

in the following integral expression for the matrix element

$$\langle x|\rho_s(t)|x'\rangle = \int dx_i dx'_i d\{x_{\omega f}\} d\{x_{\omega i}\} d\{x'_{\omega i}\} \langle x_i|\rho_s(0)|x'_i\rangle \langle \{x_{\omega i}\}|\rho_b(0)|\{x'_{\omega i}\}\rangle \tag{2.24}$$

$$\times \int D[x(\tau)]D[x'(\tau)]\mathcal{A}[x(\tau)]\mathcal{A}'[x'(\tau)] \exp\Big\{iS_0[x(\tau)] - iS_0[x'(\tau)]\Big\} \ .$$

Here we introduced two functionals $\mathcal{A}[x(\tau)]$ and $\mathcal{A}'[x'(\tau)]$ as the integrals over the bath paths

$$\mathcal{A}[x(\tau)] = \int D[\{x_\omega(\tau)\}] \exp\Big\{i\mathcal{S}[x(\tau), \{x_\omega(\tau)\}]\Big\} \ , \tag{2.25}$$

$$\mathcal{A}'[x'(\tau)] = \int D[\{x'_\omega(\tau)\}] \exp\Big\{ - i\mathcal{S}[x'(\tau), \{x'_\omega(\tau)\}]\Big\} \ . \tag{2.26}$$

The action S_0 is the action of the relevant system

$$S_0[x(\tau)] = \int_0^t d\tau \left(\frac{M}{2}\dot{x}^2(\tau) - V(x(\tau)) - x^2(\tau) \sum_\omega \frac{c_\omega^2}{2m_\omega \omega^2} \right) \ , \tag{2.27}$$

and the action $\mathcal{S}$ represents the action corresponding to the bath modes and the system-bath interaction, i.e.

$$\mathcal{S}[x(\tau), \{x_\omega(\tau)\}] = \int_0^t d\tau \sum_\omega \left(\frac{m_\omega}{2}\dot{x}_\omega^2(\tau) - \frac{m_\omega \omega^2 x_\omega^2(\tau)}{2} + c_\omega x(\tau) x_\omega(\tau) \right) \ . \tag{2.28}$$

First, we must evaluate the integrals over the bath trajectories in the expression (2.24). Since the Caldeira-Leggett Hamiltonian has square and linear dependences on the coordinate operator of the bath modes, the corresponding functional integrals (2.25) and

(2.26) are of Gaussian form. Hence they can be evaluated by means of the stationary-phase method [31, 45, 83]. Let us consider the integral $\mathcal{A}$ (Eq. (2.25)) and introduce new integration variables

$$\delta x_\omega(\tau) = x_\omega(\tau) - \bar{x}_\omega(\tau) \ , \tag{2.29}$$

where $\bar{x}_\omega$ is the stationary trajectory for the bath mode with frequency ω which can be found from the condition of the extremum of the action $\mathcal{S}$, i.e. $\delta\mathcal{S} = 0$ which leads to the following equation of motion

$$\ddot{x}_\omega(\tau) + \omega^2 x_\omega(\tau) = \frac{c_\omega}{m_\omega} x(\tau) \ . \tag{2.30}$$

The boundary conditions for the new variables now read

$$\begin{aligned} \bar{x}_\omega(0) &= x_{\omega i} \ , \qquad & \bar{x}_\omega(t) &= x_{\omega f} \ , \\ \delta x_\omega(0) &= 0 \ , \qquad & \delta x_\omega(t) &= 0 \ . \end{aligned} \tag{2.31}$$

Thus one can give the stationary trajectories $\bar{x}_\omega(\tau)$ as the solution of Eq. (2.30) in the form

$$\begin{aligned} \bar{x}_\omega(\tau) &= x_{\omega i}\frac{\sin\omega(t-\tau)}{\sin\omega t} + x_{\omega f}\frac{\sin\omega\tau}{\sin\omega t} \\ &+ \frac{c_\omega}{m_\omega\omega}\int_0^\tau ds x(s)\sin\omega(\tau-s) - \frac{c_\omega}{m_\omega\omega}\frac{\sin\omega\tau}{\sin\omega t}\int_0^t ds x(s)\sin\omega(t-s) \end{aligned} \tag{2.32}$$

and then write the functional $\mathcal{A}$ as

$$\mathcal{A}[x(\tau)] = \mathcal{A}_0 \exp\Big\{ i\mathcal{S}[x(\tau), \{\bar{x}_\omega(\tau)\}]\Big\} \ . \tag{2.33}$$

Here the action $\mathcal{S}[x(\tau), \{\bar{x}_\omega(\tau)\}]$ is taken on the stationary trajectories $\bar{x}_\omega(\tau)$ and the factor $\mathcal{A}_0$ is the functional integral over the deviations $\delta x_\omega(\tau)$ which can be evaluated by the Fourier series expansion [31]

$$\begin{aligned} \mathcal{A}_0 &= \int D[\{\delta x_\omega(\tau)\}] \exp\left[i\int_0^t d\tau \sum_\omega \left(\frac{m_\omega}{2}\delta\dot{x}_\omega^2(\tau) - \frac{m_\omega\omega^2\delta x_\omega^2(\tau)}{2} \right) \right] \\ &= \prod_\omega \sqrt{\frac{m_\omega\omega}{2\pi i \sin\omega t}} \ . \end{aligned} \tag{2.34}$$

A similar procedure can be performed with the functional $\mathcal{A}'$ which reads

$$\mathcal{A}'[x'(\tau)] = \prod_\omega \sqrt{\frac{i m_\omega\omega}{2\pi \sin\omega t}} \exp\Big\{ - i\mathcal{S}[x'(\tau), \{\bar{x}'_\omega(\tau)\}]\Big\} \ . \tag{2.35}$$

The stationary trajectories $\bar{x}'_\omega(\tau)$ in the above expression can be obtained from Eq. (2.32) replacing $x_{\omega i}$ and $x(\tau)$ by $x'_{\omega i}$ and $x'(\tau)$, respectively.

The next step is to eliminate the integration over the end points of the stationary trajectories in the expression (2.24). For this purpose we have to use the matrix elements of the initial density operator of the bath (2.10) in coordinate representation

$$
\begin{aligned}
&\langle\{x_{\omega i}\}|\rho_b(0)|\{x'_{\omega i}\}\rangle = \langle\{x_{\omega i}\}|\frac{1}{Z_b}\exp(-H_b/T_b)|\{x'_{\omega i}\}\rangle = \prod_\omega \frac{1}{x_{\omega 0}}\sqrt{\frac{\cosh(\omega/T_b)-1}{\pi\sinh(\omega/T_b)}} \\
&\times\exp\left\{\frac{x_{\omega i}x'_{\omega i}/x_{\omega 0}^2}{\sinh(\omega/T_b)} - \frac{1}{2}\left[\left(\frac{x_{\omega i}}{x_{\omega 0}}\right)^2 + \left(\frac{x'_{\omega i}}{x_{\omega 0}}\right)^2\right]\frac{\cosh(\omega/T_b)}{\sinh(\omega/T_b)}\right\}, \qquad (2.36)\\
&x_{\omega 0} = \frac{1}{\sqrt{m_\omega \omega}}\ .
\end{aligned}
$$

Finally, substituting the stationary trajectories of the bath modes (2.32) into the action $\bar{\mathcal{S}}$, using the results (2.33), (2.34) and expression (2.36) and integrating out the end points $x_{\omega i}$, $x'_{\omega i}$ and $x_{\omega f}$ in (2.24) one gets the matrix element of the reduced density operator for the relevant system in the following form

$$
\begin{aligned}
\langle x|\rho_s(t)|x'\rangle = &\int dx_i dx'_i \langle x_i|\rho_s(0)|x'_i\rangle \int D[x(\tau)]D[x'(\tau)] \\
&\times\exp\left\{iS_0[x(\tau)] - iS_0[x'(\tau)] - S_{inf}[x(\tau),x'(\tau)]\right\}\ , \qquad (2.37)
\end{aligned}
$$

where S_{inf} is the so-called Feynman-Vernon influence functional which keeps all information about the influence of the bath on the relevant system. It can be given in the form [34]

$$
\begin{aligned}
&S_{inf}[x(\tau),x'(\tau)] \qquad (2.38)\\
&= \int_0^t d\tau \int_0^\tau d\tau' \{x(\tau)-x'(\tau)\}\{K(\tau-\tau')x(\tau') - K^*(\tau-\tau')x'(\tau')\}
\end{aligned}
$$

with the influence kernel (bath correlation function)

$$
K(s) = \sum_\omega \frac{c_\omega^2 x_{\omega 0}^2}{2}\left[\coth\left(\frac{\omega}{2T_b}\right)\cos(\omega s) - i\sin(\omega s)\right]\ . \qquad (2.39)
$$

So now we got the full description of the relevant system in terms of the functional integrals of the form (2.37) which takes into account the influence of the environment exactly within the Caldeira-Leggett model. Actually the relevant system is not obligatory one particle moving in the potential $V(x)$ as it was assumed in Eq. (2.4). The main assumption is that the interaction Hamiltonian is a linear function of the bath coordinates, and only in this case we are able to eliminate the environment exactly while the operator x in H_i can be some arbitrary coordinate-dependent operator of the relevant system. Thus, one can calculate the dynamics of the relevant system by evaluating the remaining functional integral in (2.37) which is not obligatory of Gaussian form. This functional integral description will be used below for the calculation of the dissipative vibrational and population dynamics in the curve-crossing problem.

Chapter 3

Coherent-state path integrals and the damped harmonic oscillator

In this chapter we present a method for investigating the dynamics of bilinearly coupled bosonic modes based on the real-time path integrals in the coherent-state representation [41, 42, 83]. This representation has only been used as a numerical tool in a few investigations studying the propagation of wave packets [10, 15, 57] and equilibrium statistical mechanics properties [9]. Here the coherent state representation will be used in a completely analytical study. We applied this technique to the time evolution of a damped harmonic oscillator within the Caldeira-Leggett model. As far as the functional integral is of Gaussian type the stationary-phase method leads to exact results. Our goal is to diagonalize the Lagrangian allowing us to get stationary trajectories. In this way we obtain the time evolution of the reduced density matrix while similar procedures of diagonalizing the Hamiltonian used previously [73, 78] allow only to get the time evolution of the system operators.

3.1 General formalism of the real-time coherent-state path integrals

Next three subsections give an introduction into the real-time path integrals in the coherent-state representation. The dynamics of the system described by the Hamiltonian in the bosonic creation/annihilation-operator representation is considered. Using the procedure of slicing the time evolution operator into a large number of evolution operators, we will obtain the expressions for the forward and the backward path integrals. Then the case of the Gaussian integrals will be discussed.

3.1.1 Matrix element of the evolution operator

Following the treatment for the imaginary-time path integrals developed, for example, in [93] for the calculation of the partition functions, we obtain the real-time functional integral representation of the evolution operator defined in the basis of coherent states for an arbitrary bosonic Hamiltonian. The coherent states $|z\rangle$ are defined as usual for a harmonic oscillator [83]

$$|z\rangle = \sum_n \frac{z^n}{\sqrt{n!}}|n\rangle e^{-|z|^2/2}, \;\; \hat{a}|z\rangle = z|z\rangle \tag{3.1}$$

where $|n\rangle$ is the n-th eigenstate of the harmonic oscillator, $\hat{a}$ and z are the annihilation operator and its eigenvalue, respectively. In addition, we will use the completeness relation for the coherent states

$$\int \frac{dz^* dz}{\pi}|z\rangle\langle z| = 1 \; . \tag{3.2}$$

The aim is to calculate the matrix element

$$\langle\{z_\omega\}|e^{-iHt}|\{z'_\omega\}\rangle \tag{3.3}$$

where the state $|\{z_\omega\}\rangle$ denotes a product of coherent states $|z_\omega\rangle$ for all bath modes with corresponding frequencies ω. The Hamiltonian H is assumed to be normal ordered. In order to evaluate this matrix element one may, as usual, divide the time interval into N infinitesimal time slices of length ε

$$e^{-iHt} = \underbrace{e^{-iH\varepsilon}e^{-iH\varepsilon}\cdots e^{-iH\varepsilon}}_{N} \; , \tag{3.4}$$

expand each operator exponent in the small parameter ε, i.e.

$$e^{-iH\varepsilon} \approx 1 - iH\varepsilon \tag{3.5}$$

and insert the unity operator (3.2) at each dividing point. Together with the expression for the product of two coherent states

$$\langle z|z'\rangle = \exp\left[-\frac{1}{2}|z|^2 - \frac{1}{2}|z'|^2 + z^* z'\right] \tag{3.6}$$

this leads to the following form for the matrix element of the evolution operator

$$\begin{aligned}\langle\{z_\omega\}|e^{-iHt}|\{z'_\omega\}\rangle \;\; = \;\; & \prod_\omega \prod_{n=1}^{N-1}\left[\int \frac{dz^*_{\omega n} dz_{\omega n}}{\pi}\right] \\ & \times \exp\Bigg[-\sum_\omega\left(\frac{1}{2}|z_{\omega 0}|^2 + \frac{1}{2}|z_{\omega N}|^2 + \sum_{n=1}^{N-1}|z_{\omega n}|^2 - \sum_{n=1}^{N} z^*_{\omega n} z_{\omega n-1}\right) \\ & -i\sum_{n=1}^{N}\varepsilon H(\{z^*_{\omega n}\},\{z_{\omega n-1}\})\Bigg]\end{aligned} \tag{3.7}$$

with the boundary conditions

$$z_{\omega 0} = z'_\omega \; , \quad z^*_{\omega N} = z^*_\omega \; . \tag{3.8}$$

Using the identity

$$\sum_{n=1}^{N} z_n^* z_{n-1} - \sum_{n=1}^{N-1} |z_n|^2 = \frac{1}{2}(z_N^* z_{N-1} + z_1^* z_0) + \frac{\varepsilon}{2}\sum_{n=1}^{N-1}\left(z_n \frac{z_{n+1}^* - z_n^*}{\varepsilon} - z_n^* \frac{z_n - z_{n-1}}{\varepsilon}\right) \quad (3.9)$$

and performing the continuum limit in time ($\varepsilon \to 0, N \to \infty, N\varepsilon = t$) one gets the following functional integral expression for the matrix element

$$\begin{aligned} \langle\{z_\omega\}|e^{-iHt}|\{z'_\omega\}\rangle &= \prod_\tau \prod_\omega \int \frac{dz_\omega^*(\tau) dz_\omega(\tau)}{\pi} \\ &\times \exp\left[-\frac{1}{2}\sum_\omega (|z_\omega|^2 + |z'_\omega|^2) + S(\{z_\omega(\tau)\},\{z_\omega^*(\tau)\})\right] . \end{aligned} \quad (3.10)$$

Here S denotes the action depending on the trajectories $z_\omega(\tau)$ and $z_\omega^*(\tau)$

$$\begin{aligned} S(\{z_\omega(\tau)\},\{z_\omega^*(\tau)\}) &= \frac{1}{2}\sum_\omega \Big(z_\omega^*(t) z_\omega(t) + z_\omega^*(0) z_\omega(0)\Big) \\ &+ \int_0^t \left[\frac{1}{2}\sum_\omega \Big(\dot{z}_\omega^*(\tau) z_\omega(\tau) - \dot{z}_\omega(\tau) z_\omega^*(\tau)\Big) - iH(\{z_\omega^*(\tau)\},\{z_\omega(\tau)\})\right] d\tau \end{aligned} \quad (3.11)$$

which must be evaluated using the boundary conditions

$$z_\omega(0) = z'_\omega \ , \quad z_\omega^*(t) = z_\omega^* \ . \quad (3.12)$$

The form of the action (3.11) differs from the action sometimes used in the literature (for example in [16]) by the first two additional terms. Only with these terms the correct results are obtained if one employs the usual methods for calculating functional integrals [93]. We note in passing that the endpoints z_ω and z_ω^* are conjugates of each other but the trajectories $z_\omega(\tau)$ and $z_\omega^*(\tau)$ are not.

3.1.2 Forward and backward path integrals

Integrating by parts the first term under the integral in Eq. (3.11), one can write

$$S(\{z_\omega(\tau)\},\{z_\omega^*(\tau)\}) = \sum_\omega z_\omega^*(t) z_\omega(t) - \int_0^t \mathcal{L}(\{z_\omega^*(\tau)\},\{z_\omega(\tau)\}) d\tau \quad (3.13)$$

where

$$\mathcal{L}(\{z_\omega^*(\tau)\},\{z_\omega(\tau)\}) = \sum_\omega \dot{z}_\omega(\tau) z_\omega^*(\tau) + iH(\{z_\omega^*(\tau)\},\{z_\omega(\tau)\}) \ . \quad (3.14)$$

Performing a similar procedure as for the operator e^{-iHt}, for the inverse direction of time one gets

$$\begin{aligned} \langle\{z_\omega\}|e^{iHt}|\{z'_\omega\}\rangle &= \prod_\omega \prod_{n=1}^{N-1}\left[\int \frac{dz_{\omega n}^* dz_{\omega n}}{\pi}\right] \quad (3.15) \\ &\times \exp\Bigg[-\sum_\omega \left(\frac{1}{2}|z_{\omega 0}|^2 + \frac{1}{2}|z_{\omega N}|^2 + \sum_{n=1}^{N-1}|z_{\omega n}|^2 - \sum_{n=1}^{N} z_{\omega n-1}^* z_{\omega n}\right) \\ &+ i\sum_{n=1}^{N} \varepsilon H(\{z_{\omega n-1}^*\},\{z_{\omega n}\})\Bigg] , \end{aligned}$$

with the boundary conditions

$$z^*_{\omega 0} = z^*_\omega \ , \quad z_{\omega N} = z'_\omega \ . \tag{3.16}$$

Then, using the identity

$$\sum_{n=1}^{N} z^*_{n-1} z_n - \sum_{n=1}^{N-1} |z_n|^2 = \frac{1}{2}(z^*_0 z_1 + z^*_{N-1} z_N) + \frac{\varepsilon}{2} \sum_{n=1}^{N-1} \left(z^*_n \frac{z_{n+1} - z_n}{\varepsilon} - z_n \frac{z^*_n - z^*_{n-1}}{\varepsilon} \right) \tag{3.17}$$

and performing the continuum limit, for the matrix element of the evolution operator one can write

$$\langle \{z_\omega\} | e^{iHt} | \{z'_\omega\} \rangle = \prod_\tau \prod_\omega \int \frac{dz^*_\omega(\tau) dz_\omega(\tau)}{\pi}$$
$$\times \exp \left[-\frac{1}{2} \sum_\omega (|z_\omega|^2 + |z'_\omega|^2) + \tilde{S}(\{z_\omega(\tau)\}, \{z^*_\omega(\tau)\}) \right] \tag{3.18}$$

with the boundary conditions

$$z^*_\omega(0) = z^*_\omega \ , \quad z_\omega(t) = z'_\omega \tag{3.19}$$

and

$$\tilde{S}(\{z_\omega(\tau)\}, \{z^*_\omega(\tau)\}) = \sum_\omega z^*_\omega(0) z_\omega(0) + \int_0^t \mathcal{L}(\{z^*_\omega(\tau)\}, \{z_\omega(\tau)\}) d\tau \ . \tag{3.20}$$

3.1.3 Gaussian integrals. External sources and Green's function

Here we will consider the case of Gaussian functional integrals where the action has only linear and square dependence on the trajectories. Such kind of integrals can be evaluated by means of the stationary phase method. Let us consider the simplest example of a harmonic oscillator described by the Hamiltonian $H = \omega_0 a^+ a$. The action for the forward path integral $\langle a | e^{-iHt} | a' \rangle$ in this case reads

$$S = S[a(\tau), a^*(\tau)] = a^*(t) a(t) - \int_0^t \mathcal{L}(a^*(\tau), a(\tau)) d\tau \ , \tag{3.21}$$

$$\mathcal{L}(a^*(\tau), a(\tau)) = \dot{a}(\tau) a^*(\tau) + i\omega_0 a^*(\tau) a(\tau) \ . \tag{3.22}$$

The stationary phase condition $\delta S = 0$ leads to the following equations for the stationary trajectories:

$$\frac{d}{d\tau} \frac{\partial \mathcal{L}}{\partial \dot{a}(\tau)} = \frac{\partial \mathcal{L}}{\partial a(\tau)} \ ,$$
$$\frac{d}{d\tau} \frac{\partial \mathcal{L}}{\partial \dot{a}^*(\tau)} = \frac{\partial \mathcal{L}}{\partial a^*(\tau)} \ . \tag{3.23}$$

Solving Eqs. (3.23) with the boundary conditions $a(0) = a', a^*(t) = a^*$ one can see that the Lagrangian function (3.22) is zero on the stationary trajectories, and the time dependence of the action is determined by the first term on the right hand side of (3.21) depending on the end points of the trajectories

$$\langle a|e^{-iHt}|a'\rangle = \exp\left[-\frac{|a|^2}{2} - \frac{|a'|^2}{2} + a^* a' e^{-i\omega_0 t}\right] . \tag{3.24}$$

The integral over the deviations from the stationary trajectories does not depend on the end points of the stationary trajectories and equals unity.

Next, let us introduce the external sources into the action S as follows

$$S'[a(\tau), a^*(\tau)] = S[a(\tau), a^*(\tau)] + \int_0^t [j(\tau)a(\tau) + j^*(\tau)a^*(\tau)]d\tau , \tag{3.25}$$

where $j(\tau)$ and $j^*(\tau)$ are some auxiliary functions corresponding to the trajectories $a(\tau)$ and $a^*(\tau)$, respectively. Note that $j(\tau)$ and $j^*(\tau)$ are different functions, so they are not conjugated. Then, we can determine the Green's function of the harmonic oscillator at $T = 0$ as follows

$$\mathcal{G}(s, s') = \langle 0|\mathrm{T}a(s)a^+(s')|0\rangle \tag{3.26}$$

which consists of bosonic operators in the Heisenberg picture $a(s) = e^{iHs}a(0)e^{-iHs}$ and the operator T denotes time-ordering. Employing the coherent-state path integral formulation of the evolution operator one can express this Green's function with the help of the functional

$$\begin{aligned}\mathcal{G}(s, s') = &\frac{\delta}{\delta j(s)} \frac{\delta}{\delta j^*(s')} \int \frac{da da^*}{\pi} \frac{da' da'^*}{\pi} \int D[a(\tau), a^*(\tau)] \\ &\times \exp\left[-\frac{|a|^2}{2} - \frac{|a'|^2}{2} + S'[a(\tau), a^*(\tau)]\right]\Bigg|_{j=j^*=0} ,\end{aligned} \tag{3.27}$$

where the properties of coherent states Eqs. (3.1) and (3.2) have been used. Symbol $D[a(\tau), a^*(\tau)]$ in Eq. (3.27) denotes the integration over all paths $a(\tau)$ and $a^*(\tau)$, i.e.

$$D[a(\tau), a^*(\tau)] = \prod_\tau \frac{da(\tau)da^*(\tau)}{\pi} . \tag{3.28}$$

Using the stationary phase method, one can evaluate the path integral on the right hand side of Eq. (3.27). The result reads

$$\mathcal{G}(s, s') = \frac{\delta}{\delta j(s)} \frac{\delta}{\delta j^*(s')} \exp\Big(\Gamma_0[j(\tau), j^*(\tau')]\Big)\Big|_{j=j^*=0} , \tag{3.29}$$

where

$$\Gamma_0[j(\tau), j^*(\tau')] = \int_0^t d\tau \int_0^\tau d\tau' j(\tau)j^*(\tau')e^{-i\omega_0(\tau-\tau')} . \tag{3.30}$$

Calculating the functional derivatives in Eq. (3.29), for the Green's function of the harmonic oscillator one gets

$$\mathcal{G}(s,s') = \mathcal{G}(s-s') = \Theta(s-s')e^{-i\omega_0(s-s')} \ , \tag{3.31}$$

where $\Theta(s)$ is the Heavyside step function. Here we have the uncertainty at the point $s = s'$ which can be eliminated in the following way: we note that the creation operator acts on the bra-vector while the annihilation operator acts on the ket-vector in the expansion (3.5). Hence, the time dependencies of the corresponding trajectories $a(\tau)$ and $a^*(\tau)$ in the action (3.11) are always separated by a small time step ε. Because of this we should take the Green's function (3.31) in the following form

$$\mathcal{G}(s-s') = \Theta(s-s'-\varepsilon)e^{-i\omega_0(s-s')} \ . \tag{3.32}$$

The point $s = s'$ must be considered in the limit $\varepsilon \to 0$. Hence $\mathcal{G}(0) = 0$. This property of the function $\mathcal{G}$ will be used below.

3.2 Gaussian integrals. Damped harmonic oscillator

In this section the time evolution of a damped harmonic oscillator in the coherent state representation will be investigated. We will obtain the expressions for weak system-bath coupling which are easier to evaluate than those in the previous literature and which can easily be extended to a set of coupled harmonic oscillators. Since we use the Hamiltonian in the creation/annihilation-operator representation, the rotating-wave approximation (RWA) can be performed immediately by neglecting the non-rotating-wave terms. Our goal is to diagonalize the Lagrangian allowing us to get stationary trajectories. In this way we get quite simple expressions for the evolution of the reduced density matrix in the basis of coherent states for uncorrelated and correlated initial system-bath conditions, which are used for the evaluation of the expectation values of the system, in particular the population dynamics for different types of initial states of the system. One important feature of the present approach is the explicit treatment of the bath modes. As is shown below this has effects on the population dynamics already for weak system-bath interaction. The present study is quite important since the problem of coupled harmonic oscillators serves as a testbed for many dissipation theories.

3.2.1 Model Hamiltonian

First, we will introduce the Hamiltonian for one damped harmonic oscillator within the Caldeira-Leggett model Eq. (2.3) in terms of the creation/annihilation operators. The system part of the dissipative Hamiltonian represents the harmonic oscillator with the frequency ω_0

$$H_s = \omega_0 a^+ a \ . \tag{3.33}$$

The coupling between the system oscillator and the bath is considered in the coordinate-coordinate coupling model

$$H_i = \sum_\omega k_\omega (a^+ + a)(a^+_\omega + a_\omega) \tag{3.34}$$

where the k_ω are connected to the c_ω in (2.6) by

$$c_\omega = 2\sqrt{M\omega_0 m_\omega \omega} k_\omega \ . \tag{3.35}$$

In some of the following calculations we will consider the RWA which consists of neglecting the terms proportional to $a^+a^+_\omega$ and aa_ω in the interaction part of the Hamiltonian (3.34), i.e.

$$H_i^{RWA} = \sum_\omega k_\omega (a^+ a_\omega + a a^+_\omega) \ . \tag{3.36}$$

The terms $a^+a^+_\omega$ and aa_ω are associated with high frequencies $\omega_0 + \omega$ and are assumed to be very small. In Sec. 3.2.3 we will discuss the criterion of validity for the RWA.

The system-bath coupling leads to the appearance of an additional contribution to the system potential. Without the additional renormalization term H_r the system-bath coupling would lead to a dissipation-dependent shift which is undesirable. In order to cancel this contribution one introduces the renormalization term H_r of the form

$$H_r = \sum_\omega \frac{k_\omega^2}{\omega}(a + a^+)^2 \ . \tag{3.37}$$

3.2.2 Diagonalization of the Lagrangian

Next we will consider the Hamiltonian in RWA (see Eq. (3.36)) and neglect the renormalization term which is very small for small dissipation strength. The corresponding Lagrangian function (3.14) has the form

$$\begin{aligned} \mathcal{L}(\{z_\omega(\tau)\}, \{z^*_\omega(\tau)\}, a(\tau), a^*(\tau)) &= \sum_\omega \dot{z}_\omega(\tau) z^*_\omega(\tau) + \dot{a}(\tau) a^*(\tau) \\ + i\omega_0 a^*(\tau) a(\tau) + i\sum_\omega \omega z_\omega(\tau) z^*_\omega(\tau) &+ i \sum_\omega k_\omega \{a(\tau) z^*_\omega(\tau) + a^*(\tau) z_\omega(\tau)\} \end{aligned} \tag{3.38}$$

together with the boundary conditions

$$z_\omega(0) = z'_\omega \ , \quad z^*_\omega(t) = z^*_\omega \ , \tag{3.39}$$

$$a(0) = a' \ , \quad a^*(t) = a^* \ . \tag{3.40}$$

Here a (a^*) denote the system trajectories and z_ω (z^*_ω) the trajectories of the bath modes with frequency ω.

One can introduce new trajectories $A(\tau), A^*(\tau)$ using the transformations

$$a(\tau) = \sum_\Omega \alpha_\Omega A_\Omega(\tau) \ , \tag{3.41}$$

$$a^*(\tau) = \sum_\Omega \alpha_\Omega A^*_\Omega(\tau) \ , \tag{3.42}$$

$$z_\omega(\tau) = \sum_\Omega \beta_{\Omega\omega} A_\Omega(\tau) \ , \tag{3.43}$$

$$z^*_\omega(\tau) = \sum_\Omega \beta_{\Omega\omega} A^*_\Omega(\tau) \ . \tag{3.44}$$

The transformation for $a^*(\tau)(z^*_\omega(\tau))$ must be the same as for $a(\tau)(z_\omega(\tau))$ because of the symmetry of the Hamiltonian (Lagrangian) as function of $a(\tau)$ and $a^*(\tau)$ ($z_\omega(\tau)$ and $z^*_\omega(\tau)$). Substituting $a(\tau), a^*(\tau), z_\omega(\tau)$ and $z^*_\omega(\tau)$ as functions of $A(\tau)$ and $A^*(\tau)$ into the right hand side of the Lagrangian (3.38) and requiring that after the transformation the Lagrangian has to have the form

$$\mathcal{L}(\{A_\Omega(\tau)\}, \{A^*_\Omega(\tau)\}) = \sum_\Omega \dot{A}_\Omega(\tau) A^*_\Omega(\tau) + i \sum_\Omega \Omega A^*_\Omega(\tau) A_\Omega(\tau) \tag{3.45}$$

one can get the following orthogonality condition for the transformation matrix

$$\alpha_\Omega \alpha_{\Omega'} + \sum_\omega \beta_{\Omega\omega}\beta_{\Omega'\omega} = \delta_{\Omega\Omega'} \tag{3.46}$$

together with the equations for the transformation matrix coefficients

$$\omega_0 \alpha_\Omega + \sum_\omega k_\omega \beta_{\Omega\omega} = \Omega \alpha_\Omega \ , \tag{3.47}$$

$$\omega \beta_{\Omega\omega} + k_\omega \alpha_\Omega = \Omega \beta_{\Omega\omega} \ . \tag{3.48}$$

Requiring the orthogonality of the transformation and employing Eq. (3.46) one can write the back transformation as

$$A_\Omega(\tau) = \alpha_\Omega a(\tau) + \sum_\omega \beta_{\Omega\omega} z_\omega(\tau) \ , \tag{3.49}$$

$$A^*_\Omega(\tau) = \alpha_\Omega a^*(\tau) + \sum_\omega \beta_{\Omega\omega} z^*_\omega(\tau) \ . \tag{3.50}$$

Then, requiring the orthogonality again for the forward transformation we get

$$\sum_\Omega \alpha^2_\Omega = 1 \ , \tag{3.51}$$

$$\sum_\Omega \alpha_\Omega \beta_{\Omega\omega} = 0 \ , \tag{3.52}$$

$$\sum_\Omega \beta_{\Omega\omega}\beta_{\Omega\omega'} = \delta_{\omega\omega'} \ . \tag{3.53}$$

The Lagrangian (3.45) is now the Lagrangian of independent harmonic oscillators. Using the stationary phase method (i.e. the condition $\delta \int_0^t \mathcal{L} d\tau = 0$) one gets the trajectories which yield the main contribution to the functional integral of the type (3.10)

$$A_\Omega(\tau) = A_\Omega(0) e^{-i\Omega\tau} \ , \tag{3.54}$$

$$A^*_\Omega(\tau) = A^*_\Omega(0) e^{i\Omega\tau} \ . \tag{3.55}$$

Substituting this solution into the Lagrangian we see that $\mathcal{L} = 0$ on the stationary trajectories.

The last task is to find the constants $A_\Omega(0)$ and $A^*_\Omega(0)$. Using boundary conditions (3.39, 3.40), back transformation (3.49, 3.50) and solution (3.54, 3.55) one obtains

$$A_\Omega(0) = \alpha_\Omega a' + \sum_\omega \beta_{\Omega\omega} z'_\omega \ , \tag{3.56}$$

$$A^*_\Omega(0) = (\alpha_\Omega a^* + \sum_\omega \beta_{\Omega\omega} z^*_\omega) e^{-i\Omega t} \ . \tag{3.57}$$

Substituting $a(\tau), a^*(\tau), z_\omega(\tau), z^*_\omega(\tau)$ as functions of $A_\Omega(\tau)$ and $A^*_\Omega(\tau)$ into the action S (see Eq. (3.11)), using Eqs. (3.46-3.56) and taking into account that $\mathcal{L} = 0$ we obtain for the matrix element of the evolution operator

$$\begin{aligned}\langle\{z_\omega\}|\langle a|e^{-iHt}|a'\rangle|\{z'_\omega\}\rangle = \exp\Bigg[&-\frac{1}{2}|a|^2 - \frac{1}{2}|a'|^2 - \frac{1}{2}\sum_\omega |z_\omega|^2 - \frac{1}{2}\sum_\omega |z'_\omega|^2 \\ &+\xi(t) a^* a' + \sum_\omega \eta_\omega(t)(a^* z'_\omega + a' z^*_\omega) + \sum_{\omega,\omega'} \mu_{\omega,\omega'}(t) z^*_\omega z'_{\omega'}\Bigg]\end{aligned} \tag{3.58}$$

where

$$\xi(t) = \sum_\Omega \alpha^2_\Omega e^{-i\Omega t} \ , \tag{3.59}$$

$$\eta_\omega(t) = \sum_\Omega \alpha_\Omega \beta_{\Omega\omega} e^{-i\Omega t} \ , \tag{3.60}$$

$$\mu_{\omega\omega'}(t) = \sum_\Omega \beta_{\Omega\omega}\beta_{\Omega\omega'} e^{-i\Omega t} \ . \tag{3.61}$$

As one can see now we have an exponent of Gaussian type in expression (3.58) which depends on the end points only. The more general case of diagonalizing the Lagrangian beyond the RWA is given in appendix A.

3.2.3 Spectral equation. Validity range of the rotating wave approximation

The procedure of diagonalizing the Lagrangian of the interacting harmonic oscillators presented above allows us to transform the Lagrangian into a Lagrangian of independent harmonic modes. In order to investigate the properties of such a system we must know the distribution of frequencies of the new harmonic oscillators. Next we will derive the equations for the eigenfrequencies of the independent modes and then, with the help of those equations we will discuss the reduction from the non-RWA to the RWA results.

At first, consider the system-bath interaction within RWA. Having the equations (3.47) and (3.48) for the transformation matrix let us express $\beta_{\Omega\omega}$ from Eq. (3.48) as

$$\beta_{\Omega\omega} = k_\omega \frac{\alpha_\Omega}{\Omega - \omega} \tag{3.62}$$

and substitute this expression into Eq. (3.47). The equation one obtains is the equation for the eigenfrequencies of the uncoupled modes

$$\Omega - \omega_0 = \sum_\omega \frac{k_\omega^2}{\Omega - \omega} \ . \tag{3.63}$$

The same procedure can be performed for the transformation matrix without RWA. Expressing $\tilde{\alpha}_\Omega$, $\beta_{\Omega\omega}$ and $\tilde{\beta}_{\Omega\omega}$ as functions of α_Ω by using Eq. (A.10,A.11) and then substituting the obtained expressions into Eq. (A.8) with $\Omega = \Omega'$ we obtain the spectral equation without the RWA

$$(\Omega + \omega_0)(\Omega - \omega_0) = 4\omega_0 \sum_\omega \frac{k_\omega^2 \omega}{(\Omega - \omega)(\Omega + \omega)} \tag{3.64}$$

which has a quadratic dependence on the frequencies in comparison to Eq. (3.63) where the dependence is linear.

The reduction to the RWA was discussed in Ref. [78] by analysis of the time evolution of the creation and annihilation operators. Here we reduce to the RWA in terms of spectral equations and transformation matrices. Let us consider the case when the coupling constants k_ω are small. Then the right hand side of Eq. (3.64) becomes important only when Ω is close to ω_0 (for simplicity we consider only the solution of the spectral equation with positive real part). Hence we can substitute $\Omega + \omega_0$ by $2\omega_0$ on the left hand side of Eq. (3.64). On the other hand the main contribution to the sum on the right hand side comes from ω values close to Ω. Performing all replacements we get the spectral equation (3.63) within RWA.

Now consider the coefficients $\tilde{\alpha}_\Omega$ which mix the trajectories a and a^*. From Eq. (A.10) and the assumption that k_ω is small, one gets

$$\tilde{\alpha}_\Omega \simeq \alpha_\Omega \frac{\omega_0 - \Omega}{2\omega_0} \ . \tag{3.65}$$

Since $\omega_0 - \Omega \ll \omega_0$, $\tilde{\alpha}_\Omega$ can be neglected in Eqs. (A.10, A.11). The same analysis can be done for the coefficients $\tilde{\beta}_{\Omega\omega}$. After neglecting the non-RWA coefficients $\tilde{\alpha}_\Omega$ and $\tilde{\beta}_{\Omega\omega}$ Eqs. (A.10, A.11) are reduced to Eqs. (3.47) and (3.48) for the transformation matrix in RWA. An analogous procedure can be performed for the analysis of the solution of the spectral equation with negative real part. In this case the coefficients $\tilde{\alpha}_\Omega$ and $\tilde{\beta}_{\Omega\omega}$ are not small but the coefficients α_Ω and $\beta_{\Omega\omega}$ should be neglected. Actually we have to take into account both roots of the spectral equation and within the RWA we should neglect terms like $\alpha_\Omega \tilde{\alpha}_{\Omega'}$, $\alpha_\Omega \tilde{\beta}_{\Omega\omega'}$, $\tilde{\alpha}_\Omega \beta_{\Omega\omega'}$ and $\tilde{\beta}_{\Omega\omega}\beta_{\Omega'\omega'}$ (the terms $\tilde{\Lambda}, \tilde{\Delta}_\omega$ and $\tilde{\Gamma}_{\omega\omega'}$ in Eqs. (A.28, A.30, A.32)) which are non-RWA terms. As the reduction can be done only in case of weak system-bath coupling, the RWA is valid only in this case.

Next, we will obtain the renormalized spectral equation, i.e. the spectral equation for the system described by the Hamiltonian (2.3) with the counterterm (3.37). Using Eqs. (A.10, A.11) and (A.14) we get the spectral equation including the renormalization

$$\Omega^2 - \omega_0^2 - 4\omega_R\omega_0 = 4\omega_0 \sum_\omega \frac{k_\omega^2 \omega}{\Omega^2 - \omega^2} \ , \tag{3.66}$$

where the frequency ω_R is determined by Eq. (A.13). Using the identity

$$\frac{1}{\Omega - \omega + i0} = \mathcal{P}\frac{1}{\Omega - \omega} - i\pi\delta(\Omega - \omega) \tag{3.67}$$

and performing the continuum limit

$$\sum_{\omega} k_{\omega}^2 = \int d\omega g(\omega) \ , \tag{3.68}$$

where the function $g(\omega) = \sum_{\omega'} k_{\omega'}^2 \delta(\omega - \omega')$ is connected with the spectral density of the bath $J(\omega)$ as

$$J(\omega) = 2\pi M\omega_0 g(\omega) \ , \tag{3.69}$$

we can write Eq. (3.66) in the form

$$\omega_0^2 - \Omega^2 + 4\omega_0 \Delta\omega_R = 2\pi i\omega_0 g(\Omega) \ , \tag{3.70}$$

where the renormalized frequency shift is

$$\Delta\omega_R = \omega_R - \frac{1}{2}\mathcal{P}\int d\omega \frac{g(\omega)}{\Omega + \omega} + \frac{1}{2}\mathcal{P}\int d\omega \frac{g(\omega)}{\Omega - \omega} \ . \tag{3.71}$$

Let us assume that the spectral equation has a complex solution and the spectral density of the bath can be written in the form

$$g(\omega) = \frac{\gamma\omega}{2\pi\omega_0}\theta(\omega, \omega_c) \tag{3.72}$$

where $\theta(\omega, \omega_c)$ denotes the cut-off function with the cut-off frequency ω_c. In this case we can write for the frequency shift

$$\Delta\omega_R = \frac{\gamma}{2\pi\omega_0}\mathcal{P}\int d\omega \theta(\omega, \omega_c)\frac{\Omega^2}{\Omega^2 - \omega^2} \ . \tag{3.73}$$

The frequency shift in the unrenormalized spectral equation (i.e. $\omega_R = 0$) can be written as

$$\Delta\omega = \frac{\gamma}{2\pi\omega_0}\mathcal{P}\int d\omega \theta(\omega, \omega_c)\frac{\omega^2}{\Omega^2 - \omega^2} \ . \tag{3.74}$$

It is easy to see that $\Delta\omega$ increases with enlarging the cut-off frequency and $\Delta\omega$ becomes infinite when $\theta(\omega, \omega_c) = 1$, and the real part of the solution ω without counterterm goes to zero with increasing cut-off frequency, i.e. with enlarging the coupling to the high-frequency bath modes. But the renormalized frequency shift (3.73) decreases with increasing cut-off frequency. Below we will consider the case of Ohmic dissipation which is described by the following spectral density function

$$J(\omega) = M\gamma\omega \ . \tag{3.75}$$

In this case the renormalized frequency shift $\Delta\omega_R$ vanishes and the spectral equation which reads

$$\omega_0^2 - \Omega^2 = 2\pi i \omega_0 g(\Omega) \tag{3.76}$$

has the well-known solution for the classical damped harmonic oscillator

$$\Omega = \pm\sqrt{\omega_0^2 - \frac{\gamma^2}{4}} - i\frac{\gamma}{2}\ . \tag{3.77}$$

So, besides the physical reasoning for the renormalization term [103], it has to be introduced to avoid singularities in the damping problem.

3.2.4 Reduced density matrix in the coherent-state representation. Decoherence

As we are interested in a system interacting with a surrounding thermal environment, we need to calculate the reduced density operator which keeps all information about the relevant system. First, we calculate the time propagation of the reduced density matrix for the damped harmonic oscillator connected to a thermal bath which is prepared independently in the initial moment of time. Physically this means that the initial excitation of the system was faster than the time scale of the undamped motion of the system and the time of relaxation in the thermal bath.

Let us consider the density operator of the full system in the Heisenberg picture Eq. (2.12). The initial density operator is assumed to be factorized Eq. (2.22). Here we want to note in passing that the form (2.22) of the initial density operator does not mandatorily mean that the initial state is uncorrelated [78]. Below the case of correlated initial conditions will also be investigated.

We consider an initial bath with temperature T_b

$$\langle\{z_\omega\}|\rho_b(0)|\{z'_\omega\}\rangle = \frac{1}{Z_b}\exp\left[-\frac{1}{2}\sum_\omega |z_\omega|^2 - \frac{1}{2}\sum_\omega |z'_\omega|^2 + \sum_\omega e^{-\omega/T_b} z^*_\omega z'_\omega\right] \tag{3.78}$$

and a system with arbitrary initial conditions determined by the function $f_0(a_1^*, a_2)$

$$\langle a_1|\rho_s(0)|a_2\rangle = \exp\left[-\frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} + f_0(a_1^*, a_2)\right]\ . \tag{3.79}$$

Using the identity

$$\int \frac{dzdz^*}{\pi} e^{-\varsigma|z|^2 - \delta z} f(z^*) = \frac{1}{\varsigma} f\left(\frac{\delta}{\varsigma}\right) \tag{3.80}$$

which is valid for any integral of Gaussian type, employing our RWA-result (3.58) and tracing out the bath, one obtains the matrix element of the reduced density operator in the integral form

$$\langle a|\rho_s(t)|a'\rangle = F(T_b,t)\int \frac{da_1 da_1^*}{\pi}\frac{da_2 da_2^*}{\pi}\exp\left[-\frac{|a|^2}{2}-\frac{|a'|^2}{2}-|a_1|^2-|a_2|^2+f_0(a_1^*,a_2)\right.$$
$$\left.+\frac{\xi}{1+Q}a^*a_1+\frac{\xi^*}{1+Q}a_2^*a'+\frac{Q}{1+Q}a^*a'+(1-\frac{|\xi|^2}{1+Q})a_1a_2^*\right] , \qquad (3.81)$$

where

$$Q(t,T_b)=\sum_\omega |\eta_\omega(t)|^2 n_\omega , \qquad n_\omega=\frac{1}{e^{\omega/T_b}-1} . \qquad (3.82)$$

The details of the procedure of elimination of the bath are given in Appendix B. The function $F(t,T_b)$ is an unknown function coming from the integration over the end points of the bath trajectories and can be determined from the normalization condition $\mathrm{Tr}\rho=1$, yielding

$$1=F(T_b,t)(1+Q)\int\frac{da_1^*da_1}{\pi}\exp(f_0(a_1^*,a_1)-|a_1|^2)$$
$$=F(T_b,t)(1+Q)\mathrm{Tr}(\rho_s(0))=F(T_b,t)(1+Q) . \qquad (3.83)$$

In order to evaluate the function $\xi(t)$ defined in Eq. (3.59) we will use the method proposed in [98]. Using Eq. (3.63), identity (3.67) and performing the continuum limit (3.68) we get an equation for the eigenfrequencies

$$\Omega-\omega_0=\mathcal{P}\int d\omega\frac{g(\omega)}{\Omega-\omega}-i\pi g(\Omega) . \qquad (3.84)$$

Then, using Eq. (3.46) for $\Omega=\Omega'$, Eq. (3.62) and noting that

$$1+\sum_\omega\frac{k_\omega^2}{(\Omega-\omega)^2}=\frac{d}{d\Omega}\left(\Omega-\omega-\sum_\omega\frac{k_\omega^2}{\Omega-\omega}\right) \qquad (3.85)$$

we can write $\xi(t)$ in integral form

$$\xi(t)=\sum_\Omega\alpha_\Omega^2e^{-i\Omega t}=\frac{1}{2\pi i}\int_\infty^{-\infty}d\Omega\frac{e^{-i\Omega t}}{\Omega-\tilde{\omega}(\Omega)+i\pi g(\Omega)} \qquad (3.86)$$

where

$$\tilde{\omega}(\Omega)=\omega_0+\mathcal{P}\int d\omega\frac{g(\omega)}{\Omega-\omega} . \qquad (3.87)$$

The residues of this integral are determined by equation (3.63) for the eigenfrequencies. So the function $\xi(t)$ is the Green's function of the full system, and the poles of its Fourier transform determine the eigenfrequencies of the system. Using Eq. (3.81) one finds that the Green's function $\xi(t)$ and its conjugate $\xi^*(t)$ determine the time evolution of the mean values of the annihilation and creation operators, respectively, as

$$\langle a(t)\rangle = \langle a(0)\rangle\xi(t) , \qquad (3.88)$$

$$\langle a^+(t)\rangle = \langle a^+(0)\rangle\xi^*(t) \ . \tag{3.89}$$

As was shown in Sec. 3.2.3, the RWA leads to correct results only in case of weak system-bath coupling. In this limit one can replace Ω by ω_0 in the expressions for $\tilde{\omega}$ and $g(\Omega)$. The Green's function $\xi(t)$ then reads

$$\xi(t) = e^{-i\tilde{\omega}(\omega_0)t-\pi g(\omega_0)t} \ . \tag{3.90}$$

The function $Q(t, T_b)$ in this case is given by

$$Q(t, T_b) = n_{\omega_0}(1 - |\xi(t)|^2) \ . \tag{3.91}$$

In order to confirm the correctness of expression (3.81) let us calculate the relaxation of the mean value of the occupation number for the system

$$\langle n_s(t)\rangle = Q(t, T_b) + n_s(0)|\xi(t)|^2 \ . \tag{3.92}$$

If we consider Ohmic dissipation Eq. (3.75), using Eq. (3.69) we can write [98]

$$\langle n_s(t)\rangle = n_s(0)e^{-\gamma t} + n_{\omega_0}(1 - e^{-\gamma t}) \ , \tag{3.93}$$

where $\gamma \ll \omega_0$ should be fulfilled.

The functions $\xi(t)$ and $\xi^*(t)$ represent the connection between the initial and final points of the trajectories in expression (3.81) and hence describe the process of decoherence of the system. For time $t = \infty$ using Eq. (3.90) one gets $\xi(t = \infty) = \xi^*(t = \infty) = 0$, i.e. the system looses the information about its initial state. The final state of the system after the decoherence is determined by the function $Q(t = \infty) = n_{\omega_0}$. The matrix element of the reduced density matrix at $t = \infty$ reads

$$\begin{aligned} \langle a|\rho_s(t=\infty)|a'\rangle &= \frac{1}{Z_s}\exp\left[-\frac{|a|^2}{2} - \frac{|a'|^2}{2} + e^{-\omega_0/T_b}a^*a'\right] \ , \\ Z_s &= \frac{1}{1 - e^{-\omega_0/T_b}} \end{aligned} \tag{3.94}$$

which exactly corresponds to the system described by the density operator $\rho = \frac{1}{Z_s}e^{-\omega_0 a^+ a/T_b}$.

Formula (3.81) together with Eqs. (3.90,3.91) can be used for the calculation of the mean value of observables. One has to express the initial state of the system as well as the operator of the observable via coherent states with the help of Eq. (3.1) and evaluate the integrals over the end points of the trajectories in Eq. (3.81) using Eq. (3.80). As an example we calculate the evolution of the level populations. Assuming that the system initially is in its n-th eigenstate, one gets for the evolution of the m-th level

$$\begin{aligned} \langle m|\rho(t)|m\rangle &= \frac{1}{n!m!}\frac{\partial^m\partial^n}{\partial\zeta_1^m\partial\zeta_2^n} \\ &\times \frac{1}{(1+(1-\zeta_1)Q(t,T_b))(1-\zeta_2)+\zeta_2|\xi(t)|^2(1-\zeta_1)}\Bigg|_{\zeta_1=\zeta_2=0} \ , \end{aligned} \tag{3.95}$$

where the ζ_1 and ζ_2 are only auxiliary variables. The population dynamics is discussed in more details below.

3.2.5 Dynamics of the Gaussian wave packet. Population dynamics

Here we consider the relaxation in a system initially prepared in a pure state with some wave function $|\psi\rangle$. The initial state of the bath is an equilibrium state with temperature T_b. For the calculation of the time evolution of the system we will use Eq. (A.22) together with Eqs. (A.23-A.26) and (A.27-A.32). Then, we consider the non-RWA terms (A.28,A.30,A.32) as a perturbation (i.e. the coupling strength has to be small enough). The calculations presented below have been done to first order in this perturbation. For simplicity Ohmic damping (3.75) has been assumed.

First we will determine the time evolution of a Gaussian wave packet with width σ and peak position x_0, i.e.

$$\rho_s(0) = |\psi_0(x)\rangle\langle\psi_0(x)| \tag{3.96}$$

where

$$|\psi_0(x)\rangle = |\psi(x, t = 0)\rangle = \frac{1}{\sqrt{\sqrt{\pi}\sigma}} \exp\left[-\frac{(x - x_1)^2}{2\sigma^2}\right] . \tag{3.97}$$

For simplicity, we set the initial momentum to zero. The unit of measurement for x, x_0 and σ is $1/\sqrt{M\omega_0}$. In Fig. 3.1 the matrix element of the reduced density operator in coordinate representation $P(x,t) = \langle x|\rho_s(t)|x\rangle$ is shown for four different initial wave packets and temperatures. One can see that the width of the wave packet oscillates with time if the initial width is smaller or larger than $1/\sqrt{M\omega_0}$ (upper left and right plots of Fig. 3.1, respectively). The damping time for the peak position coordinate $\bar{x}$ of the wave packet is larger than the time in which the width of the wave packet changes from its initial value to the equilibrium one. Note that the wave packet keeps its Gaussian form during the time evolution.

The time evolution of the coherent state (i.e. $\sigma = 1$) within the RWA at $T_b = 0$ has the form

$$\begin{aligned} P(x, \sigma = 1) &= \frac{1}{\sqrt{\pi}} \exp\left[(x - \bar{x})^2\right] , \\ \bar{x} = x_0 \mathrm{Re}(\xi(t)) &= x_0 \cos(\Omega_0 t) \exp(-\Omega_1 t) , \end{aligned} \tag{3.98}$$

where Ω_0 and Ω_1 are the real and imaginary parts of the solution of the spectral equation (3.63), respectively. This behaviour is shown in the lower left plot of Fig. 3.1. Although Eq. (3.98) implies the existence of a non-dissipative coherent state in RWA, it was shown already [78], that they can only exist at zero temperature and in systems that meet the conditions for the RWA.

At time $t = \infty$ the function $P(x)$ can be written as

$$P(x) = \frac{1}{\sqrt{\pi}\sigma_f} \exp\left(-\frac{x^2}{\sigma_f^2}\right) \tag{3.99}$$

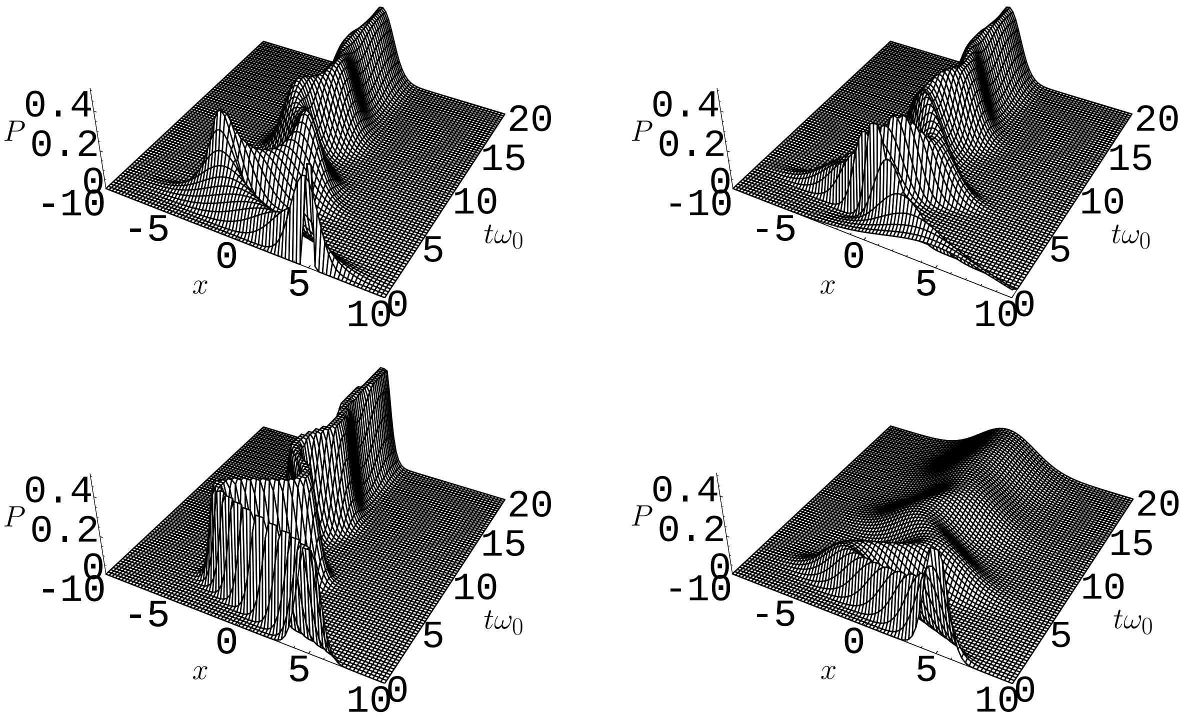

Figure 3.1: Evolution of $P(x,t)$. $\sigma = 0.2, T_b = \omega_0$ (upper left figure), $\sigma = 5, T_b = \omega_0$ (upper right figure), $\sigma = 1, T_b = 0$ (lower left figure), $\sigma = 1, T_b = 5\omega_0$ (lower right figure), $x_1 = 5, \gamma = 0.2\omega_0$ (for all figures).

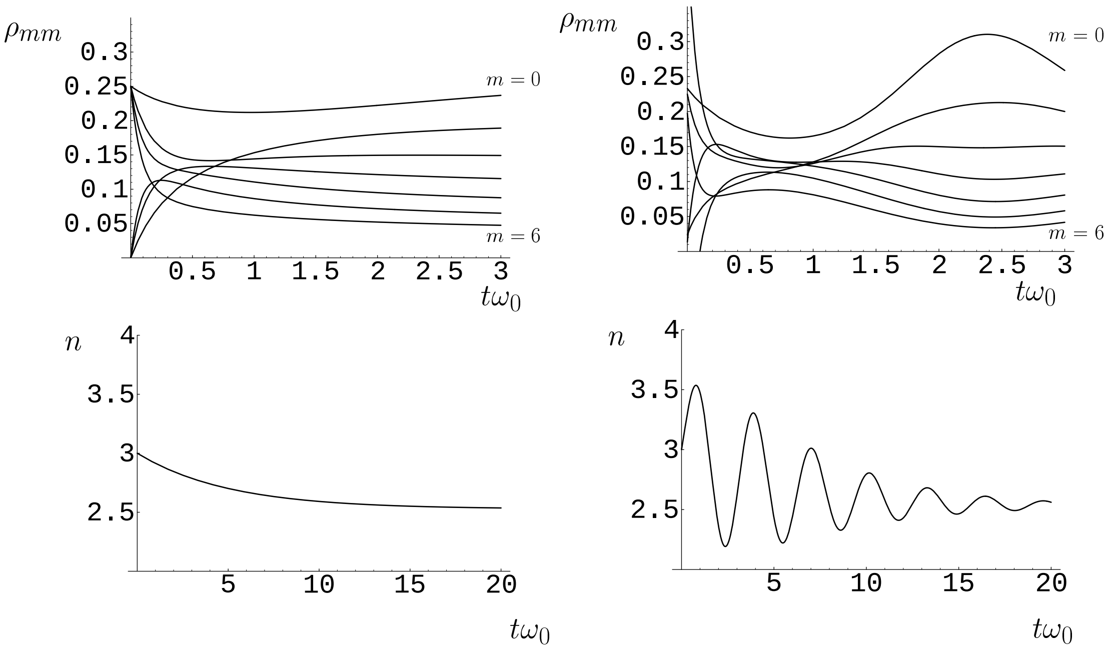

Figure 3.2: Evolution of the population $\rho_{mm}(t)$ of the first seven levels ($m = 0, 1, ..., 6$) and the mean value of the occupation number $n(t)$ starting from the mixed initial state of the system $\rho_s(0) = 0.25|0\rangle\langle 0| + 0.25|2\rangle\langle 2| + 0.25|4\rangle\langle 4| + 0.25|6\rangle\langle 6|$ (left figure) and from the pure initial state of the system $|\psi(0)\rangle = 0.5|0\rangle + 0.5|2\rangle + 0.5|4\rangle + 0.5|6\rangle$ (right figure).
$T_b = 3\omega_0, \gamma = 0.2\omega_0$. Note that in the levels with $m > 6$ there is also some population at this value of temperature.

where the final width σ_f is

$$\sigma_f = \sqrt{1 + 2Q(T_b, t = \infty)}\ . \tag{3.100}$$

In the high temperature limit of the bath one gets $\sigma_f^2 \sim T_b$ as was shown before [34]. The spreading of Gaussian wave packet in accordance with the formula (3.100) is plotted in the lower right plot of Fig. 3.1.

Next, in Fig. 3.2 the time evolution of the populations of the system oscillator and the corresponding mean occupation numbers are shown. We considered the cases of a mixed and a pure initial state of the system. The difference between the populations with pure and mixed initial states is due to the influence of the non-RWA terms in the presence of coherence in the case of a pure initial state. The unphysical results at $t = 0+$ in Fig. 3.2 in case of the pure initial state are the consequence of jolts in the domain $0 < t < 1/\omega_c$ due to the factorized initial conditions, as was discussed by many authors (see, for example, [78] and references therein). In case of uncorrelated initial conditions the changes in the system at the beginning of the system-bath interaction are mostly determined by the fast decoherence of the system where the time scale of decoherence is $\tau_d \sim 1/\omega_c$. In our case $\omega_c = \infty$ and therefore the instantaneous changes (initial jolts) of the population occur. In spite of this, the mean occupation number has the correct value at $t = 0+$.

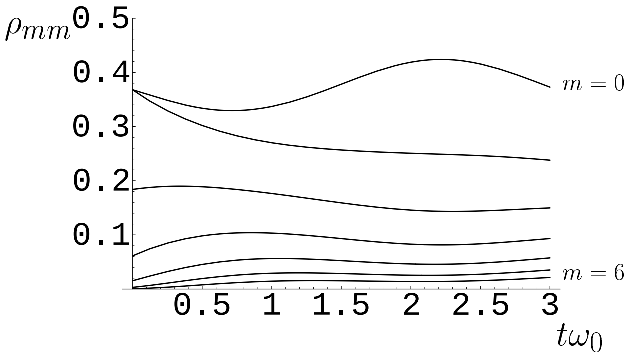

Figure 3.3: Evolution of the population of first seven levels ($m = 0, 1, ..., 6$) starting from the coherent initial state of the system $|\psi(0)\rangle = |a\rangle, |a|^2 = 1$. $T_b = 3\omega_0, \gamma = 0.2\omega_0$.

Finally, in Fig. 3.3 we plotted the population dynamics of a system initially prepared in a coherent state $|a\rangle$ with $|a|^2 = 1$. In spite of the presence of coherence for this initial state one can observe relatively weak influence of non-RWA terms and an absence of the initial jolts. One can check using the formula $\rho_{m,m}(0) = \frac{|a|^{2m}}{m!} e^{-|a|^2}$ for the initial state that the level populations have the correct values at $t = 0$. Since the uncertainty relation is minimized in coherent states the behaviour of the system at $t \approx 0$ is close to a classical one whereas the initial jolts caused by the fast initial decoherence appear to be purly a quantum effect.

3.2.6 Correlated initial system-bath conditions

In this subsection we consider the influence of the initial correlations on the evolution of the mean value of the system coordinate. Let us suppose that the relevant system and the bath initially are in an equilibrium state with the temperature T, but the relevant vibrational mode is on a shifted harmonic potential surface, i.e.

$$V(x) = \frac{M\omega_0^2 (x + x_1)^2}{2} \ . \tag{3.101}$$

Thus, the full system at the time $t < 0$ is described by the Hamiltonian

$$\tilde{H} = H + q(a^+ + a) \ , \tag{3.102}$$

where $q = \omega_0 x_1/\sqrt{2} x_0$, $x_0 = 1/\sqrt{M\omega_0}$, and H is determined by Eq. (2.3). Here we will restrict ourself to the RWA. The time evolution of the matrix element of the reduced density matrix is calculated in Appendix C in the case $T = 0$. The result reads

$$\begin{aligned} & \text{limit}_{\lambda\to\infty} \langle a| e^{-iHt} e^{-\lambda\tilde{H}} e^{iHt} |a'\rangle & (3.103) \\ = \ & \exp\Big[-\frac{|a|^2}{2} - \frac{|a'|^2}{2} - \varepsilon(t) a^* - \varepsilon^*(t) a' - |\varepsilon(t)|^2 \Big] \ , & \end{aligned}$$

$$\varepsilon(t) = q \sum_\Omega \frac{\alpha_\Omega^2}{\Omega} e^{-i\Omega t} \ , \tag{3.104}$$

$$\varepsilon^*(t) = q \sum_\Omega \frac{\alpha_\Omega^2}{\Omega} e^{i\Omega t} \ . \tag{3.105}$$

In order to show the influence of the initial correlations let us calculate the evolution of the mean value of the system coordinate

$$\langle x(t)\rangle = \frac{x_0}{\sqrt{2}}\langle a(t) + a^*(t)\rangle = -\frac{x_0}{\sqrt{2}}(\varepsilon(t) + \varepsilon^*(t)) \ . \tag{3.106}$$

The function $\varepsilon(t)$ and its conjugate $\varepsilon^*(t)$ determine the time evolution of the annihilation and creation operators, respectively, and converge to the functions $\frac{q}{\omega_0}\xi(t)$ and $\frac{q}{\omega_0}\xi^*(t)$, respectively, if γ in Eq. (3.75) is very small. This can be seen by comparing Eq. (3.103) and Eq. (3.81) with the initial condition $f_0(a_1^*, a_2) = \frac{q}{\omega_0}(a_1^* + a_2)$ and $T_b = 0$. Calculating $\varepsilon(t)$ and $\varepsilon^*(t)$ in the same manner as the Green's function $\xi(t)$, in case of weak Ohmic dissipation one gets

$$\langle x(t)\rangle = -x_1\frac{\omega_0\,\tilde{\omega}}{\tilde{\omega}^2 + (\gamma/2)^2}\left(\cos\tilde{\omega}t + \frac{\gamma}{2\tilde{\omega}}\sin\tilde{\omega}t\right)e^{-\gamma t/2} \ , \tag{3.107}$$

where $\tilde{\omega} = \tilde{\omega}(\omega_0)$ is determined by Eq. (3.87). One can see that the trajectory determined by Eq. (3.107) is a classical trajectory which can be obtained for the damped harmonic oscillator only by using the correlated initial system-bath conditions [78]. The initial mean value of momentum is zero for the considered initial state, $\frac{d\langle x(t)\rangle}{dt}\Big|_{t=0} = 0$ as it should be, while for the mean value $\bar{x}$ from Eq. (3.98) obtained without initial correlations this condition is not satisfied.

3.2.7 Summary

In this chapter we have introduced an alternative treatment for the investigation of systems described by Hamiltonians with bilinear and quadratic terms and we applied this method to the problem of one harmonic oscillator coupled to a heat bath. In contrast to the well known Feynman-Vernon influence-functional approach described in Chapter 2 we did non eliminate the bath but canceled the system-bath interaction by diagonalization of the Lagrangian. In this way one can obtain spectral equations for the system of interest which have been investigated in this chapter.

In contrast to a similar procedure of diagonalizing the Hamiltonian which was used in [78] and allows one to get the time evolution of the creation and annihilation operators, the present treatment gives the time evolution of the reduced density matrix and therefore leads to the full description of the relevant system. Furthermore, it allows us to consider a non-equilibrium bath and, therefore, correlated initial system-bath conditions. This consideration is normally not possible within the treatments which are based on the master equations. Besides of this, our method gives a quite simple expression (3.81) for the reduced density matrix in RWA which can be easily used for further evaluation of the expectation values of observables, although even in the first order of non-RWA terms the calculations turned out to be quite unwieldy.

The proposed approach was tested for simple factorized initial conditions when the bath initially is in thermal equilibrium with an arbitrary temperature, and for correlated initial conditions when the relevant system initially is in thermal equilibrium with the bath but on a shifted potential. Instead of Langevin-like equations for the trajectories of the relevant system in the influence functional method we have a multi-dimensional integral over the end points of the trajectories. The calculation method for such integrals is shown in the case of RWA. The influence of non-RWA terms like $\tilde{\Lambda}, \tilde{\Delta}_\omega, \tilde{\Gamma}_{\omega\omega'}$ becomes evident in the population dynamics with pure initial system conditions in absence of initial correlations. In first order of the perturbative treatment in the system-bath coupling the non-RWA terms are proportional to the coupling parameter γ in case of Ohmic dissipation (3.75), and in the presence of coherence in the initial system state they lead to initial jolts in the population. But in case of a system initially prepared in a coherent state the initial jolts disappear since the system behaves almost classically at the beginning of the evolution.

Chapter 4

Dissipative vibrational dynamics in curve-crossing systems

In this chapter we consider the curve-crossing dynamics describing electron transfer in a dissipative environment which is one of the interesting examples of dissipative quantum dynamics [4, 6]. The most well-known electron transfer theory is the rate theory by Marcus [58, 59] and its improvements [39, 94]. At the time of their development these rate theories were considered break-throughs but meanwhile they cannot describe all the available experimental data anymore. In recent years experimentalists were able to monitor the time development during the electron transfer processes using ps and fs laser systems [22, 24, 48, 79, 99, 106, 107]. To describe the observed oscillatory behavior for such short times rate theories are not sufficient.

The system of interest is a quantum mechanical two-level system representing electronic states coupled to a dissipative reaction coordinate. If the vibrational degrees of freedom introduced by the reaction coordinate are neglected, i.e. if only two electronic states coupled to a heat bath are treated the model is called spin-boson model [52, 53, 103]. It has been investigated intensively [25, 35, 49]. The method presented in this chapter is based on the path integral formulation for the vibrational dynamics, i.e. including vibrational levels. The exact numerical method of calculating these path integrals is developed in Ref. [97].

Here we construct a perturbation theory in a small coordinate shift between the potential energy surfaces and investigate the dynamics of a Gaussian wave packet within this perturbative treatment. This is done without restriction to weak system-bath coupling or weak intercenter coupling. Such a small shift between the potential energy surfaces is often found for systems in the Marcus inverted region. In these systems the potential minimum of the upper potential energy surface is higher in energy than the lower potential energy surface at that point of the reaction coordinate. A well-known example is the electron transfer in betaine-30 [48, 82, 100].

The most known treatment allowing the path integral formulation of the two-level system is the non-interacting blip approximation [52] which is based on the formal expansion in powers of the adiabatic coupling between two electronic states. In the present contribution we use the mapping approach [84, 89, 95] in order to rewrite the Lagrangian function for the discrete electronic system in terms of continuous degrees of freedom. The mapping approach allows us to describe a two-level system by bosonic creation/annihilation operators. The path integral for these new bosonic modes is written in the coherent-state representation while we use the usual Feynman integrals in the phase-space representation for the path integral over the vibronic trajectories. The bath is eliminated using the Feynman-Vernon method. The non-Gaussian part of the remaining system path integral which appears due to the coupling between electronic and vibrational subsystems is treated perturbatively as mentioned above. Finally, the evolution of a Gaussian wave packet and of its peak position is calculated to first order in this perturbation theory.

4.1 Model Hamiltonian and mapping approach

In order to describe the dissipative curve-crossing dynamics we will use the well-known Hamiltonian for electron transfer [33] within the system-plus-bath model

$$H = H_s + H_b + H_i + H_r \ , \tag{4.1}$$

where the system is described by

$$H_s = \frac{p^2}{2M} + |1\rangle\langle 1|U_1(x) + |2\rangle\langle 2|(U_2(x) - \Delta G^0) + \Delta(|1\rangle\langle 2| + |2\rangle\langle 1|) \ . \tag{4.2}$$

Here the reaction coordinate is denoted by x ($p = -i\frac{d}{dx}$), the electronic states by $|1\rangle, |2\rangle$ and the corresponding potential energy surfaces by $U_1(x), U_2(x)$ (see Fig. 1). The difference in energy between the minima of the two potential energy surfaces or, more precisely, of the two free energy surfaces is denoted by ΔG^0 [4]. The last term in Eq. (4.2) describes the intercenter coupling with coupling strength Δ which is assumed to be independent of the reaction coordinate x. The Hamiltonians of a bath H_b and system-bath interaction H_i are determined within the standard Caldeira-Leggett model by Eqs. (2.5) and (2.6), respectively. In case of harmonic potential energy surfaces with equal curvature (see Fig. 4.1) and by setting the minimum energy of the left potential to zero, one can write the total Hamiltonian H in the form

$$H = \epsilon|2\rangle\langle 2| + \Delta(|1\rangle\langle 2| + |2\rangle\langle 1|) - \omega_0\frac{x_s x}{x_0^2}|2\rangle\langle 2| + H_{\rm CL}, \tag{4.3}$$

where $H_{\rm CL}$ is a Hamiltonian of Caldeira-Leggett type [52]

$$H_{\rm CL} = \frac{p^2}{2M} + \frac{M\omega_0^2 x^2}{2} + H_i + H_b + H_r, \tag{4.4}$$

and

$$\epsilon = \frac{M\omega_0^2 x_s^2}{2} - \Delta G^0, \qquad x_0 = \frac{1}{\sqrt{M\omega_0}}. \tag{4.5}$$

Here the identity for the electronic part $|1\rangle\langle 1| + |2\rangle\langle 2| = 1$ has been used.

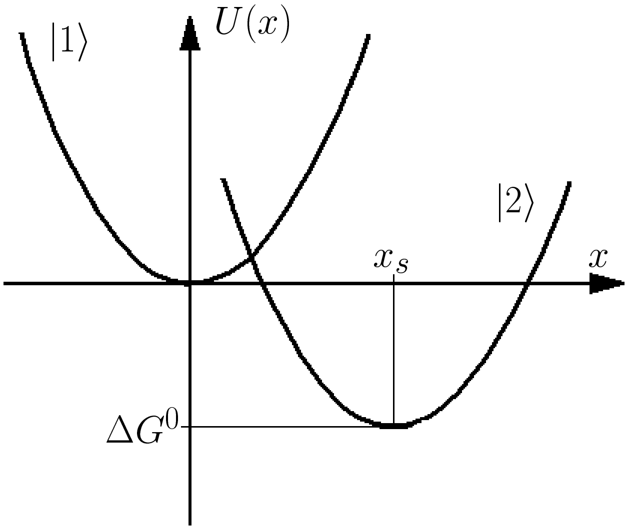

Figure 4.1: Potential energy surfaces for the reaction coordinate x.

Next, in order to determine the Lagrangian function for the electronic degrees of freedom we rewrite the Hamiltonian of the electronic part of the system in terms of continuous degrees of freedom [84, 89, 95]. Using the bosonic creation/annihilation operators a_n^+, a_m $(n, m = 1, 2)$ yields the mapping relations

$$|n\rangle\langle m| \rightarrow a_n^+ a_m, \tag{4.6}$$

$$|n\rangle \rightarrow |1\rangle_n |0\rangle_m. \tag{4.7}$$

Equation (4.6) represents an exact mapping of the discrete quantum variables onto continuous degrees of freedom. Let us rewrite the Hamiltonian (4.3) in terms of the new operators a_n^+, a_m

$$H = \epsilon a_2^+ a_2 + \Delta(a_1^+ a_2 + a_2^+ a_1) - \omega_0 \frac{x_s x}{x_0^2} a_2^+ a_2 + H_{\mathrm{CL}}. \tag{4.8}$$

Now instead of two coupled quantum states we have a system of bilinearly coupled harmonic oscillators. Only the ground and the first excited state of them must be taken into account. The Hamiltonian of the form (4.8) will be considered below.

4.2 Path integral in combined coherent-state and phase-space representation

As the Hamiltonian (4.8) is represented by creation/annihilation operators as well as by operators acting in phase-space, we will use both representations for the formulation of the path integral. Our purpose is to calculate the dynamics of a wave packet, i.e. its probability density $P(x, t)$ as function of coordinate x and time t

$$P(x, t) = \langle x|\mathrm{Tr}_{el}\mathrm{Tr}_b \rho(t)|x\rangle\ , \tag{4.9}$$

where Tr_{el} and Tr_b denote the trace over the electronic states $|1\rangle, |2\rangle$ and the trace over the bath states, respectively. First, let us write the expression for the matrix element of the evolution operator $\exp(-iHt)$ [31, 93]

$$\begin{aligned}&\langle a_1|_1\langle a_2|_2\langle x_f|\langle\{x_{\omega f}\}|e^{-iHt}|\{x_{\omega i}\}\rangle|x_i\rangle|a_2'\rangle_2|a_1'\rangle_1 \\ &= \int D[\{a_n(\tau)\},\{a_n^*(\tau)\}]D[x(\tau)]D[\{x_\omega(\tau)\}] \\ &\times \exp\left[iS[x,\{x_\omega\}] + S_{el}[\{a_n\},\{a_n^*\}] - \frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2}\right]\end{aligned} \tag{4.10}$$

where

$$\begin{aligned}S[x,\{x_\omega\}] &= \int_0^t d\tau\left[\frac{M\dot{x}^2(\tau)}{2} - \frac{M\omega_0^2x^2(\tau)}{2} + \omega_0\frac{x_s}{x_0^2}x(\tau)a_2^*(\tau)a_2(\tau)\right. \\ &\left.+\sum_\omega\left(\frac{m_\omega\dot{x}_\omega^2(\tau)}{2} - \frac{m_\omega\omega^2x_\omega^2(\tau)}{2} + c_\omega x(\tau)x_\omega(\tau) - x^2(\tau)\frac{c_\omega^2}{2m_\omega\omega^2}\right)\right],\end{aligned} \tag{4.11}$$

The action of the electronic subsystem has the form

$$\begin{aligned}&S_{el}[\{a_n\},\{a_n^*\}] = a_1^*(t)a_1(t) + a_2^*(t)a_2(t) - \int_0^t d\tau\mathcal{L}_{el}(\tau), \\ &\mathcal{L}_{el}(\tau) = \dot{a}_1(\tau)a_1^*(\tau) + \dot{a}_2(\tau)a_2^*(\tau) + i\epsilon a_2^*(\tau)a_2(\tau) + i\Delta(a_1^*(\tau)a_2(\tau) + a_2^*(\tau)a_1(\tau))\ .\end{aligned} \tag{4.12}$$

Here $|a_n\rangle$ denotes coherent states, i.e. eigenstates of the annihilation operator a_n. The end points of the trajectories for the actions (4.11,4.12) are

$$x(0) = x_i, \qquad x_\omega(0) = x_{\omega i}, \tag{4.13}$$

$$x(t) = x_f, \qquad x_\omega(t) = x_{\omega f}, \tag{4.14}$$

and for the electronic trajectories

$$a_n(0) = a_n', \qquad a_n^*(t) = a_n^*. \tag{4.15}$$

For the inverse direction of time, i.e. for the matrix element of the operator $\exp(iHt)$ one can write

$$\begin{aligned}&\langle a_1|_1\langle a_2|_2\langle x_i|\langle\{x_{\omega i}\}|e^{iHt}|\{x_{\omega f}\}\rangle|x_f\rangle|a_2'\rangle_2|a_1'\rangle_1 \\ &= \int D[\{a_n(\tau)\},\{a_n^*(\tau)\}]D[x(\tau)]D[\{x_\omega(\tau)\}] \\ &\times \exp\left[-iS[x,\{x_\omega\}] + \tilde{S}_{el}[\{a_n\},\{a_n^*\}] - \frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2}\right]\ .\end{aligned} \tag{4.16}$$

The action S for the vibrational mode (Eq. (4.11)) as well as the end points (4.13, 4.14) remain the same. But the action for the electronic trajectories now reads

$$\tilde{S}_{el}[\{a_n\},\{a_n^*\}] = a_1^*(0)a_1(0) + a_2^*(0)a_2(0) + \int_0^t d\tau\mathcal{L}_{el}(\tau), \tag{4.17}$$

where the Lagrangian function $\mathcal{L}_{el}(\tau)$ is the same as in Eq. (4.12) and must be evaluated with the boundary conditions

$$a_n(t) = a_n', \qquad a_n^*(0) = a_n^*. \tag{4.18}$$

The above expressions will be evaluated in the next sections.

4.3 Reduced density matrix for the relevant vibrational mode

In the following we restrict ourselves to the time propagation of the reduced density matrix (4.9) in case of factorized initial system-bath conditions. The bath is initially assumed to be in a thermal equilibrium state with temperature T_b and its initial density matrix in the coordinate representation has the form (2.36). The Gaussian wave packet is prepared in the left potential surface at time $t = 0$ (see Fig. 4.1). Thus, the initial state of the relevant system (electronic system plus vibrational mode) is given by the density matrix

$$\rho_s(0, x_i, x_i') = |\psi_0(x_i)\rangle |0\rangle_2 |1\rangle_1 \langle 1|_1 \langle 0|_2 \langle \psi_0(x_i')| \tag{4.19}$$

where the initial wave function of the vibrational coordinate $\psi_0(x)$ is described by Eq. (3.97). Using the procedure for the elimination of the bath within the Feynman-Vernon approach [31] discussed in Chapter 2 and taking into account the results of the previous section, one gets for the probability density (4.9)

$$\begin{aligned} P(x,t) = \prod_{\alpha=1}^{3}\prod_{i=1}^{2}\int \frac{da_{i\alpha}da_{i\alpha}^*}{\pi} a_{12}^* a_{13} \int D[\{a_n(\tau)\},\{a_n^*(\tau)\}]D[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}]\Phi \times \\ \times \exp\Big(-\sum_{n=1}^{2}\sum_{\beta=1}^{3}|a_{n\beta}|^2 + S_{el}[\{a_n(\tau)\},\{a_n^*(\tau)\}] + \tilde S_{el}[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}]\Big) \end{aligned} \tag{4.20}$$

Here the functional Φ describes the dissipative vibrational mode and the electronic-vibronic coupling

$$\begin{aligned} \Phi &= \Phi[t, x, a_2(\tau), a_2^*(\tau), \tilde a_2(\tau), \tilde a_2^*(\tau)] \\ &= \int dx_i dx_i' \psi_0(x_i)\psi_0(x_i') \int_{x(0)=x_i}^{x(t)=x} D[x(\tau)] \int_{x'(0)=x_i'}^{x'(t)=x} D[x'(\tau)] e^{\Sigma}, \end{aligned} \tag{4.21}$$

$$\begin{aligned} \Sigma &= \Sigma[x(\tau), x'(\tau), a_2(\tau), a_2^*(\tau), \tilde a_2(\tau), \tilde a_2^*(\tau)] = iS_0[x(\tau)] - iS_0[x'(\tau)] \\ &\quad - S_{inf}[x(\tau), x'(\tau)] + iS_{v-el}[x(\tau), x'(\tau), a_2(\tau), a_2^*(\tau), \tilde a_2(\tau), \tilde a_2^*(\tau)], \end{aligned} \tag{4.22}$$

The actions of the electronic subsystem S_{el} and $\tilde S_{el}$ are given by Eqs. (4.12) and (4.17), respectively, the action S_{v-el} represents the interaction between the vibrational mode x and the electronic subsystem

$$S_{v-el} = \int_0^t d\tau \frac{\omega_0 x_s}{x_0^2}\Big(x(\tau)a_2^*(\tau)a_2(\tau) - x'(\tau)\tilde a_2^*(\tau)\tilde a_2(\tau)\Big), \tag{4.23}$$

S_0 is the action of the pure vibrational mode, i.e.

$$S_0[x(\tau)] = \int_0^t d\tau \left(\frac{M\dot x^2(\tau)}{2} - \frac{M\omega_0^2 x^2(\tau)}{2} - x^2(\tau)\sum_\omega \frac{c_\omega^2 x_{\omega 0}^2}{2\omega}\right). \tag{4.24}$$

The first index of the creation/annihilation operator eigenvalues $a_{n\alpha}^*/a_{n\alpha}$ in Eq. (4.20) corresponds to the number of the potential energy surface, the second one numerates the different variables of integration for one and the same electronic state.

All information about the influence of the bath is now kept in the influence functional S_{inf} of the form (2.38). In correspondence with Eqs. (4.15) and (4.18) the electronic trajectories $a_n(\tau)$, $a_n^*(\tau)$ and $\tilde{a}_n(\tau)$, $\tilde{a}_n^*(\tau)$ must satisfy the boundary conditions

$$\begin{aligned} a_n(0) &= a_{n2}, & a_n^*(t) = a_{n1}^*, \\ \tilde{a}_n(t) &= a_{n1}, & \tilde{a}_n^*(0) = a_{n3}^* \ . \end{aligned} \tag{4.25}$$

Next, for convenience let us to introduce new variables for the vibrational mode

$$r(\tau) = \frac{1}{2}(x(\tau) + x'(\tau)), \qquad q(\tau) = x(\tau) - x'(\tau) \ . \tag{4.26}$$

In these new variables the action Σ from Eq. (4.22) takes the form

$$\begin{aligned} \Sigma &= i \int_0^t d\tau [M\dot{q}(\tau)\dot{r}(\tau) - M\tilde{\omega}^2 q(\tau)r(\tau) + r(\tau)Q_-(\tau) + q(\tau)Q_+(\tau)] \\ &+ \int_0^t d\tau \int_0^\tau d\tau' [iM\gamma(\tau - \tau')q(\tau)r(\tau') - \xi(\tau - \tau')q(\tau)q(\tau')] \end{aligned} \tag{4.27}$$

where $\gamma(\tau)$ is the damping kernel

$$\gamma(\tau) = \frac{1}{M} \sum_\omega x_{0\omega}^2 c_\omega^2 \sin(\omega\tau), \tag{4.28}$$

and

$$\xi(\tau) = \frac{1}{2} \sum_\omega x_{0\omega}^2 c_\omega^2 \coth \frac{\omega}{2T_b} \cos(\omega\tau), \tag{4.29}$$

$$Q_-(\tau) = \frac{\omega_0 x_s}{x_0^2}(a_2^*(\tau)a_2(\tau) - \tilde{a}_2^*(\tau)\tilde{a}_2(\tau)), \tag{4.30}$$

$$Q_+(\tau) = \frac{1}{2}\frac{\omega_0 x_s}{x_0^2}(a_2^*(\tau)a_2(\tau) + \tilde{a}_2^*(\tau)\tilde{a}_2(\tau)) \ . \tag{4.31}$$

The presence of the counterterm in the Hamiltonian leads to the renormalization of the frequency of the vibrational mode. The renormalized frequency reads

$$\tilde{\omega}^2 = \omega_0^2 + \frac{1}{M} \sum_\omega \frac{x_{0\omega}^2 c_\omega^2}{\omega}. \tag{4.32}$$

4.4 Vibronic generating functional

In this section we will calculate the functional $\Phi(t, x)$ of the electronic trajectories $a_2(\tau), a_2^*(\tau), \tilde{a}_2(\tau), \tilde{a}_2^*(\tau)$, Eq. (4.21), as a path integral over the vibrational trajectories $x(\tau), x'(\tau)$. Here we can treat the functions Q_- and Q_+ from Eqs. (4.30,4.31) as some auxiliary functions playing the role of external sources, and the functional

$\Phi[t, x, Q_-(\tau), Q_+(\tau)]$ now is the generating functional of the dissipative vibrational mode for the special initial vibronic conditions (4.19). Since the integral in Φ is Gaussian, it can be evaluated by means of the stationary phase method. As usually, in this way the integral (4.21) turns into the product

$$\Phi[t, x, Q_-(\tau), Q_+(\tau)] = \mathcal{P}(t) \int dx_i dx_i' \psi_0(x_i)\psi_0(x_i') e^{\bar{\Sigma}} \ , \tag{4.33}$$

where $\bar{\Sigma} = \Sigma[\bar{r}(\tau), \bar{q}(\tau), Q_-(\tau), Q_+(\tau)]$ is the action taken on the stationary trajectories $\bar{r}(\tau)$ and $\bar{q}(\tau)$, and the prefactor $\mathcal{P}(t)$ is the integral over the deviations $\delta r(\tau) = r(\tau) - \bar{r}(\tau)$ and $\delta q(\tau) = q(\tau) - \bar{q}(\tau)$. The condition for the extremum of the action $\delta\Sigma = 0$ leads to the following equations for the stationary trajectories

$$\ddot{\bar{q}}(\tau) + \tilde{\omega}^2 \bar{q}(\tau) + \int_\tau^t d\tau' \gamma(\tau - \tau')\bar{q}(\tau') = \frac{Q_-(\tau)}{M}, \tag{4.34}$$

$$\begin{aligned} \ddot{\bar{r}}(\tau) + \tilde{\omega}^2 \bar{r}(\tau) - \int_0^\tau d\tau' \gamma(\tau - \tau')\bar{r}(\tau') = Q_0(\tau) \\ = \frac{Q_+(\tau)}{M} + \frac{i}{M} \int_0^t d\tau' \xi(\tau - \tau')\bar{q}(\tau'). \end{aligned} \tag{4.35}$$

Taking into account the boundary conditions (4.13, 4.14) for the vibrational trajectories, which in the new variables read

$$\begin{aligned} \bar{q}(0) &= x_i - x_i', & \bar{q}(t) &= 0, \\ \bar{r}(0) &= \frac{1}{2}(x_i + x_i'), & \bar{r}(t) &= x, \end{aligned} \tag{4.36}$$

and using the Laplace transformation method one can give the solution of Eqs. (4.34) and (4.35) as

$$\begin{aligned} \bar{q}(\tau) &= (x_i - x_i')\frac{G(t-\tau)}{G(t)} + \frac{1}{M}\int_\tau^t d\tau' G(\tau' - \tau) Q_-(\tau') \\ &\quad - \frac{G(t-\tau)}{MG(t)} \int_0^t d\tau' G(\tau') Q_-(\tau'), \end{aligned} \tag{4.37}$$

$$\begin{aligned} \bar{r}(\tau) &= \frac{1}{2}(x_i + x_i')\left[\dot{G}(\tau) - G(\tau)\frac{\dot{G}(t)}{G(t)}\right] + x\frac{G(\tau)}{G(t)} \\ &\quad + \int_0^\tau d\tau' G(\tau - \tau') Q_0(\tau') - \frac{G(\tau)}{G(t)} \int_0^t d\tau' G(t - \tau') Q_0(\tau') \end{aligned} \tag{4.38}$$

where $G(\tau)$ is the Green's function for one damped harmonic oscillator and its Laplace transform $\hat{G}(p)$ reads [34]

$$\hat{G}(p) = \int_0^\infty G(\tau) e^{-p\tau} d\tau = \frac{1}{p^2 + \tilde{\omega}^2 - \hat{\gamma}(p)} \ , \tag{4.39}$$

$$\hat{\gamma}(p) = \int_0^\infty \gamma(\tau) e^{-p\tau} d\tau \ .$$

Then, using the equations for the stationary trajectories again, one can write the action Σ at the extremum point in the form

$$\bar{\Sigma}[\bar{r}(\tau), \bar{q}(\tau), Q_-(\tau), Q_+(\tau)] = iM\dot{\bar{r}}(t)\bar{q}(t) - iM\dot{\bar{r}}(0)\bar{q}(0)$$
$$+i\int_0^t d\tau Q_-(\tau)\bar{r}(\tau) + \int_0^t d\tau \int_0^\tau d\tau' \xi(\tau - \tau')\bar{q}(\tau)\bar{q}(\tau') \ . \tag{4.40}$$

The next step is to substitute the solution (4.37,4.38) into the action (4.40) and integrate over the end points x_i and x_i' of the vibronic trajectories in Eq. (4.33) using the expression for the initial wave function (3.97). After that one finds for the functional Φ

$$\Phi[t, x, Q_-(\tau), Q_+(\tau)] = \frac{2\sqrt{\pi}\mathcal{P}(t)}{\sigma\sqrt{\lambda_0\lambda_1}} \exp\left[-\frac{(x - R_0)^2}{\tilde{\sigma}^2}\right] e^{\Lambda} \ , \tag{4.41}$$

where

$$\tilde{\sigma} = \sigma\sqrt{\lambda_0\lambda_1 \frac{G(t)}{M}} \ , \tag{4.42}$$

$$\lambda_0 = \frac{1}{4\sigma^2} + \int_0^t d\tau \int_0^t d\tau' \xi(\tau - \tau') \frac{G(t-\tau)G(t-\tau')}{2G^2(t)}, \tag{4.43}$$

$$\lambda_1 = \frac{4}{\sigma^2} + \frac{1}{\lambda_0}\left(M\frac{\dot{G}(t)}{G(t)}\right)^2 , \tag{4.44}$$

$$R_0 = \frac{\sigma^2}{2}\dot{G}(t)\left(R_+ - \frac{2x_1}{\sigma^2}\right) + \frac{\tilde{\sigma}^2}{2}R_- - i\frac{G(t)}{M}\phi_1 \ , \tag{4.45}$$

$$R_+ = i\int_0^t d\tau Q_-(\tau)\left[\dot{G}(\tau) - \frac{\dot{G}(t)}{G(t)}G(\tau)\right] , \tag{4.46}$$

$$R_- = i\int_0^t d\tau Q_-(\tau)\frac{G(\tau)}{G(t)}, \tag{4.47}$$

$$\phi_1 = i\int_0^t d\tau Q_+(\tau)\frac{G(t-\tau)}{G(t)} - \int_0^t d\tau \int_0^t d\tau' \xi(\tau - \tau')G(t-\tau)R(\tau'), \tag{4.48}$$

$$R(\tau) = \frac{1}{M}\int_\tau^t d\tau' G(\tau' - \tau)Q_-(\tau') - \frac{G(t-\tau)}{MG(t)}\int_0^t d\tau' G(\tau')Q_-(\tau'). \tag{4.49}$$

Now we can see that the result (4.41) presents the time evolution of the Gaussian wave packet with time-dependent width $\tilde{\sigma}(t)$ and peak position $R_0[Q_-, Q_+, t]$. The exponential factor Λ is a functional of the sources Q_- and Q_+ and a function of time but not a function of x.

$$\begin{aligned}\Lambda[t, Q_-(s), Q_+(s)] &= -ix_1 \int_0^t ds Q_-(s)\dot{G}(s) + \frac{i}{M}\int_0^t ds \int_0^s ds' G(s-s')Q_-(s)Q_+(s') \\ &\quad - \int_0^t ds \int_0^t ds' R(s,s')Q_-(s)Q_-(s') \ , \end{aligned} \tag{4.50}$$

$$\begin{aligned}R(s,s') &= \frac{\sigma^2}{4}\dot{G}(s)\dot{G}(s') + \frac{1}{4M^2\sigma^2}G(s)G(s') \\ &\quad + \frac{1}{2M^2}\int_0^s d\tau \int_0^{s'} d\tau' G(s-\tau)G(s'-\tau')\xi(\tau-\tau') \ . \end{aligned} \tag{4.51}$$

Since the external sources Q_- and Q_+ in (4.30, 4.31) were introduced into the functional Φ by the action (4.23) which has linear dependence on the trajectories $x(\tau)$ and $x'(\tau)$, the path integral over the deviations $\mathcal{P}(t)$ does not depend on the Q_- and Q_+. Hence it can be found from the normalization condition $\int_{-\infty}^{\infty} dx \Phi[x, t, Q_- = 0, Q_+ = 0] = 1$. Finally, the result (4.41) reads

$$\Phi[t, x, Q_-(\tau), Q_+(\tau)] = \frac{1}{\sqrt{\pi}\tilde{\sigma}} \exp\left[-\frac{(x-R_0)^2}{\tilde{\sigma}^2}\right] e^{\Lambda} \ . \tag{4.52}$$

Integrating this result over the coordinate x, i.e. tracing out the vibrational mode, one gets

$$\Phi_0[t, Q_-(\tau), Q_+(\tau)] = \int_{-\infty}^{\infty} dx \Phi[t, x, Q_-(\tau), Q_+(\tau)] = e^{\Lambda} \ . \tag{4.53}$$

So it is possible to say that the first factor $(1/(\sqrt{\pi}\tilde{\sigma}))\exp[-(x-R_0)^2/\tilde{\sigma}^2]$ in (4.52) is responsible for the dissipative dynamics of the wave packet while the factor Φ_0 is the pure vibronic generating functional. It describes the influence of the vibrational system on the electronic one in terms of the determination (4.30, 4.31) due to the electronic-vibronic coupling (4.23).

4.5 Perturbation theory and generating functional approach

In this section we will calculate the probability density $P(x,t)$ in the case of small coordinate shift x_s between the potential energy surfaces, i.e.

$$x_s \ll x_0 \ . \tag{4.54}$$

The above condition shall lead to a small non-Gaussian contribution compared to the Gaussian part of the integral (4.20). So either ϵ or Δ have to be of the order of or larger than the frequency of the harmonic oscillators ω_0. One can see that the functional Φ represents the non-Gaussian part of the functional integral over the electronic trajectories (4.20). As the functions $Q_+(t)$ and $Q_-(t)$ are proportional to x_s (see Eqs. (4.30, 4.31)), we calculate the contribution from the functional $\Phi[t, x, a(\tau), a^*(\tau), \tilde{a}(\tau), \tilde{a}^*(\tau)]$ perturbatively in the small parameter x_s in accordance with the condition (4.54). In order to calculate the contribution from the non-Gaussian terms in $P(x,t)$ the generating functional approach [45] will be used. As a first step one has to calculate the electronic generating functional, i.e. the path integral (4.20) with $\Phi = 1$ introducing external sources $j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)$ into the action in Eq. (4.20) as

$$S'_{el}[\{a_n\},\{a_n^*\}] = S_{el}[\{a_n\},\{a_n^*\}] + \int_0^t d\tau (a_2(\tau) j(\tau) + a_2^*(\tau) j^*(\tau)) \tag{4.55}$$

and

$$\tilde{S}'_{el}[\{\tilde{a}_n\},\{\tilde{a}_n^*\}] = \tilde{S}_{el}[\{\tilde{a}_n\},\{\tilde{a}_n^*\}] + \int_0^t d\tau (\tilde{a}_2(\tau) \tilde{j}(\tau) + \tilde{a}_2^*(\tau) \tilde{j}^*(\tau)) \ . \tag{4.56}$$

This functional integral is of Gaussian type and can be calculated with the help of the stationary phase method. Using the coherent-state path integral technique described in the third chapter of this thesis, after some calculations one gets for the generating functional

$$\begin{aligned} \Xi[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)] &= \Big[1 + J_1[j] J_1^*[j^*] + J_1[\tilde{j}] J_1^*[\tilde{j}^*] + J_1[j] J_1^*[\tilde{j}^*] \\ &\times \int_0^t d\tau \int_0^t d\tau' j^*(\tau) \tilde{j}(\tau') (e^{i\Omega_1(\tau-\tau')} \cos^2\varphi + e^{i\Omega_2(\tau-\tau')} \sin^2\varphi)\Big] \exp\left(\Gamma[j,j^*] + \Gamma^*[\tilde{j}^*, \tilde{j}]\right) \end{aligned} \tag{4.57}$$

with

$$\Omega_1 = \frac{\Delta}{\upsilon}, \qquad \Omega_2 = \epsilon - \frac{\Delta}{\upsilon}, \tag{4.58}$$

$$\cos\varphi = \frac{1}{\sqrt{1+\upsilon^2}}, \quad \sin\varphi = \frac{\upsilon}{\sqrt{1+\upsilon^2}}, \tag{4.59}$$

$$\upsilon = \sqrt{\left(\frac{\epsilon}{2\Delta}\right)^2 + 1} - \frac{\epsilon}{2\Delta}. \tag{4.60}$$

The details of this calculation and determinations of the functionals Γ and J_1 are given in appendix D. Next, in order to calculate the contribution from the functional Φ in Eq. (4.20) one has to perform the replacements

$$a_2(\tau) \to \frac{\delta}{\delta j(\tau)}, \quad a_2^*(\tau) \to \frac{\delta}{\delta j^*(\tau)}, \tag{4.61}$$

$$\tilde{a}_2(\tau) \to \frac{\delta}{\delta \tilde{j}(\tau)}, \quad \tilde{a}_2^*(\tau) \to \frac{\delta}{\delta \tilde{j}^*(\tau)} \tag{4.62}$$

in the expressions Eq. (4.30,4.31) for $Q_+(t)$ and $Q_-(t)$. Now we have the formal expression for the probability density

$$P(x,t) = \Phi(x,t)\Xi(t) \tag{4.63}$$

where Φ is the operator $\Phi\left[x, t, \frac{\delta}{\delta j(\tau)}, \frac{\delta}{\delta j^*(\tau)}, \frac{\delta}{\delta \tilde{j}(\tau)}, \frac{\delta}{\delta \tilde{j}^*(\tau)}\right]\Big|_{j=j^*=\tilde{j}=\tilde{j}^*=0}$ acting on the generating functional $\Xi[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)]$.

4.6 Dynamics of the reaction coordinate

The purpose of the present section is to describe the calculation of the probability density $P(x,t)$ and the mean value of $x(t)$ to first order in x_s/x_0. Note that the population of the electronic states which would be more easily accessible in experiment is determined by the functional $\Phi_0 = e^{\Lambda}$ (4.53). In this functional the vibrational mode x was traced out and the exponential factor Λ has square dependence in the expansion parameter x_s/x_0 (except the first term in (4.50)). Thus the perturbation expansion for the electronic population is of second order in the small parameter x_s/x_0. But the leading term in the vibrational dynamics turns out to be of first order in x_s/x_0. So here we restrict ourselves to the calculation of the leading term of the perturbation expansion in x_s/x_0.

The assumption (4.54) can also be written as

$$\frac{x_s^2}{x_0^2} \ll \frac{\Delta G^0}{\omega_0} \;, \tag{4.64}$$

if the energy shift ΔG^0 is of the order of or larger than the frequency ω_0. Hence, the results given by our perturbation theory are valid in particular in the Marcus inverted region where Eq. (4.64) is satisfied. But because of Eq. (4.54) the reorganization energy $E_r = M\omega_0^2 x_s^2/2 = (x_s/x_0)^2\omega_0/2$ has to be smaller than the frequency of the system oscillators ω_0 and the present first-order treatment is therefore not applicable to systems with very large reorganization energies as, for example, in Ref. [19]. In all configurations of the examples discussed below the reorganization energy is small enough.

The leading term of the perturbation expansion of the functional Φ is the functional R_0 from Eq. (4.45). This functional is of the first order in x_s since it has linear dependence on the functions Q_- and Q_+. So the mean value of the vibrational coordinate is determined as follows

$$\langle x(t)\rangle = R_0\left[t, \frac{\delta}{\delta j(\tau)}, \frac{\delta}{\delta j^*(\tau)}, \frac{\delta}{\delta \tilde{j}(\tau)}, \frac{\delta}{\delta \tilde{j}^*(\tau)}\right] \Xi[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)]\Big|_{j=j^*=\tilde{j}=\tilde{j}^*=0} . \tag{4.65}$$

Let us perform the replacements (4.61 ,4.62) in the Eqs. (4.30,4.31) and calculate the results of the action of the operators Q_- and Q_+ on the electronic generating functional Ξ (4.57). Here we have to use the relations

$$\frac{\delta^2}{\delta j(s)\delta j^*(s)}\Gamma[j(\tau), j^*(\tau')] = 0 \;, \qquad \frac{\delta^2}{\delta \tilde{j}(s)\delta \tilde{j}^*(s)}\Gamma^*[\tilde{j}^*(\tau), \tilde{j}(\tau')] = 0 \tag{4.66}$$

where the functional Γ is determined by Eq. (D.7) and the property (3.32) of the Green's function of the harmonic oscillator was used. Finally one gets

$$Q_-\left[t, \frac{\delta}{\delta j(\tau)}, \frac{\delta}{\delta j^*(\tau)}, \frac{\delta}{\delta \tilde{j}(\tau)}, \frac{\delta}{\delta \tilde{j}^*(\tau)}\right] \Xi[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)]\Big|_{j=j^*=\tilde{j}=\tilde{j}^*=0} = 0 \;, \tag{4.67}$$

$$\begin{aligned} Q_+\left[t, \frac{\delta}{\delta j(\tau)}, \frac{\delta}{\delta j^*(\tau)}, \frac{\delta}{\delta \tilde{j}(\tau)}, \frac{\delta}{\delta \tilde{j}^*(\tau)}\right] \Xi[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)]\Big|_{j=j^*=\tilde{j}=\tilde{j}^*=0} \\ = \frac{\omega_0 x_s}{x_0^2}\frac{\delta^2}{\delta j(\tau)\delta j^*(\tau)} J_1[j(\tau)] J_1^*[j^*(\tau)]\Big|_{j=j^*=\tilde{j}=\tilde{j}^*=0} \;, \end{aligned} \tag{4.68}$$

where the functional J_1 is given by Eq. (D.5). Evaluating the functional derivative on the right hand side in Eq. (4.68) we obtain the following expression for the mean value of vibrational coordinate

$$\langle x(t)\rangle = x_1\dot{G}(t) + 2x_s\omega_0^2\left(\frac{\Delta}{h}\right)^2\int_0^t d\tau G(t-\tau)[1-\cos h\tau]\ . \tag{4.69}$$

The frequency h in Eq. (4.69) is the Rabi frequency describing the Rabi oscillations in the two-level system

$$h = \Omega_2 - \Omega_1 = -\sqrt{\epsilon^2 + (2\Delta)^2}\ . \tag{4.70}$$

In a similar perturbative manner one gets the probability density $P(x,t)$ in the form

$$P(x,t) = \frac{1}{\sqrt{\pi}\tilde{\sigma}}\exp\left[-\frac{(x-\langle x(t)\rangle)^2}{\tilde{\sigma}^2}\right]\ . \tag{4.71}$$

The first term in Eq. (4.69) represents the well-known result for a single damped harmonic oscillator [34] while the second term describes the electron transfer dynamics. Note, that in the first order of x_s the evolution of the mean value of x does not depend on the temperature of the bath. Since the second term in Eq. (4.69) is the convolution of the Green's function of the damped harmonic oscillator and the oscillating function describing nondissipative Rabi oscillations in the electronic subsystem, the damping in the dynamics of the reaction coordinate in first order of the present perturbation theory is described by the direct influence of the bath through the function $G(s)$. As the dynamics of the electronic subsystem does not depend on the sign of x_s, the influence of the vibrational degrees of freedom on the population dynamics must appear only in the second order of this perturbation theory. As it has been mentioned above, this influence is described by the functional Λ which is of second order in the parameter x_s and has been neglected here. In the next chapter we will consider the dissipative population dynamics evaluating the contribution of the functional Λ.

In the expression (4.71) for the evolution of the Gaussian wave packet the width $\tilde{\sigma}$ of the wave packet is determined by the dynamics within a single harmonic potential energy surface and does not depend on x_s while the peak position $\langle x(t)\rangle$ defined by Eq. (4.69) includes the influence of the coupling to the other potential energy surface. Below the case of Ohmic dissipation with infinite cut-off frequency (3.75) is considered. The Green's function $G(t)$ in this case is given by [34] (see also Appendix E for the details)

$$G(t) = \frac{\sin(\Omega_0 t)}{\Omega_0}\exp[-\gamma t/2], \tag{4.72}$$
$$\Omega_0 = \sqrt{\omega_0^2 - \gamma^2/4}\ .$$

In Figs. 4.2 and 4.3 the evolution of the mean value (4.69) of the reaction coordinate x of the wave packet (3.97) is compared with the results of Redfield theory within Markov approximation [7, 60, 76]. The initial wave packet is located on the left potential energy surface and is centered at the minimum of the parabola. The comparison is done for

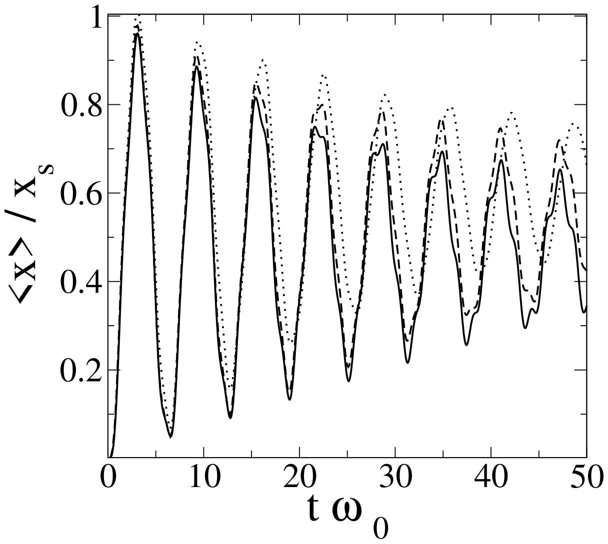

Figure 4.2: Evolution of the mean value of the reaction coordinate x for an initially unshifted Gaussian wave packet ($x_1 = 0$) within perturbation theory Eq. (4.69) (solid line) and Redfield theory for $x_s = 0.4x_0$ (dashed line) and for $x_s = 0.8x_0$ (dotted line). $\Delta G^0 = \omega_0, \Delta = 2\omega_0, \gamma = 0.05\omega_0$. Note that for the present perturbative method $\langle x \rangle / x_s$ does not depend on x_s and therefore only one curve for this approach is shown.

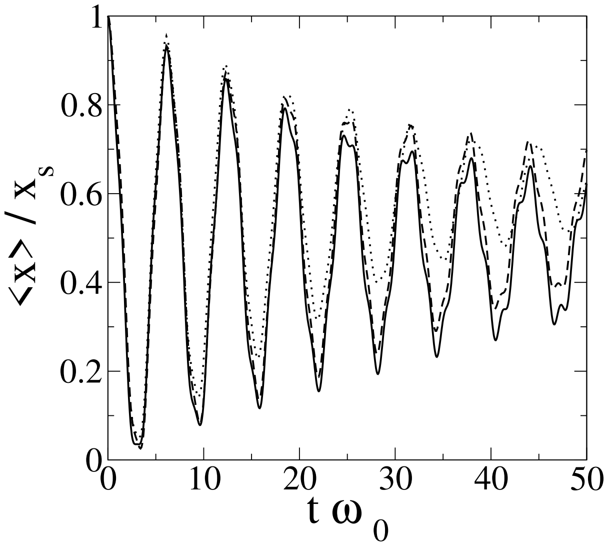

Figure 4.3: Same as Fig. 4.2, but for an initially shifted wave packet ($x_1 = x_s$).

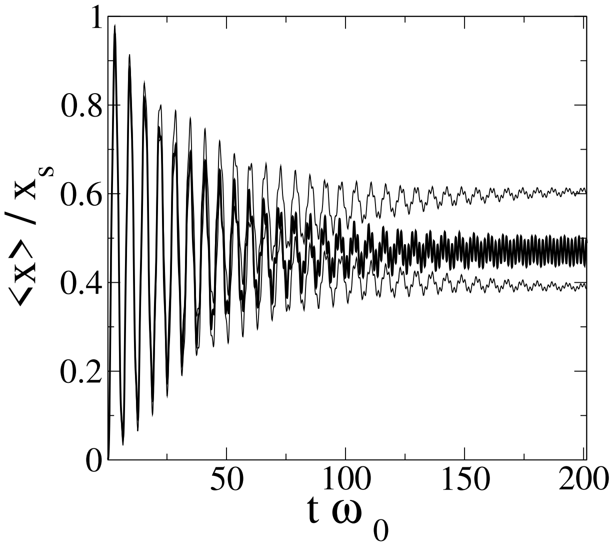

Figure 4.4: Evolution of the mean value of the reaction coordinate x for an initially unshifted Gaussian wave packet ($x_1 = 0$): results of Eq. (4.69) (middle curve) with $\epsilon = 1$ and Redfield results with $\Delta G^0 = \omega_0$ (upper curve) and $\Delta G^0 = -\omega_0$ (lower curve). The shift between the potential energy surfaces is $x_s = 0.4x_0$, the other parameters are the same as in Fig. 4.2.

different values of the intercenter shift x_s in case of weak system-bath coupling, i.e. within the range of validity of the Redfield theory. As we kept only the first-order terms in the perturbation expansion, the result for the dimensionless value $\langle x \rangle / x_s$ given by Eq. (4.69) does not depend on x_s. Hence there is only one curve for the present perturbative method in Figs. 4.2 and 4.3 independent of x_s. One can observe relatively good agreement between the result given by Eq. (4.69) and the results of the Redfield method up to times of about $t\omega_0 \sim 30$. For times $t\omega_0 > 30$ the deviations increase. This is a consequence of the influence of higher-order perturbation terms. Accordingly, the deviations are significantly larger for larger values of x_s. If the initial wave packet is centered at the minimum of the left parabola the next term of the perturbation theory is of third order while for an initially shifted wave packet the next term is of second order. The results of our first-order perturbation theory and the Redfield method approaching thermal equilibrium ($t \to \infty$) are shown in Fig. 4.4. The difference between the Redfield results at $t\omega_0 \gg 1$ with $\Delta G^0 = \omega_0$ and $\Delta G^0 = -\omega_0$ is due to the presence of the reorganization energy in the expression for the energy shift ϵ which is described by the first term in Eq. (4.5). This term is of second order in the coordinate shift x_s and is therefore neglected within our first-order perturbation treatment. So the terms of first order do not depend on the sign of ΔG^0. We should also note that the higher-order terms of the perturbation theory depend on temperature through the function ξ (Eq. (4.29)). These terms become larger with increasing temperature T_b. In case of large temperature $T_b \gg \omega_0$ the presented perturbation theory fails to give accurate results. Taking higher order terms of the present

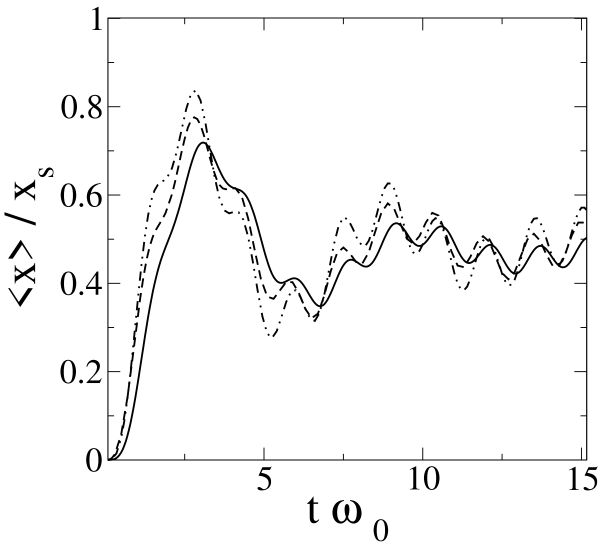

Figure 4.5: Evolution of the mean value of the reaction coordinate x for an initially unshifted Gaussian wave packet ($x_1 = 0$): result of Eq. (4.69) (solid line), Redfield theory with Markov approximation (dashed line) and without Markov approximation (dash-dotted line). The shift between the potential energy surfaces is $x_s = 0.1x_0, \gamma = 0.5\omega_0$, and the other parameters are the same as in Fig. 4.2.

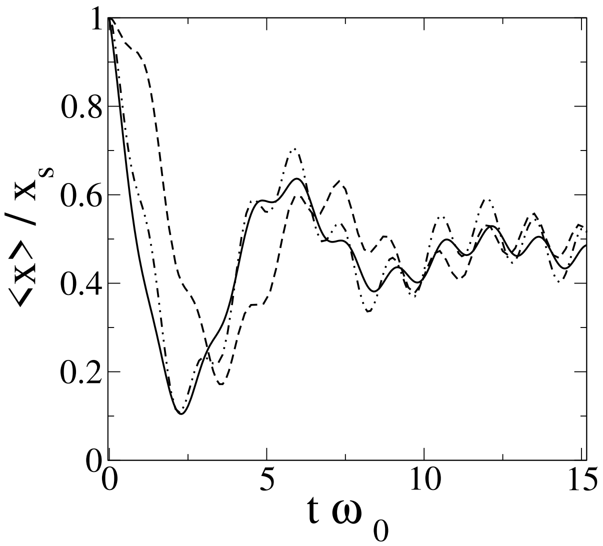

Figure 4.6: Same as Fig. 4.5, but for an initially shifted wave packet ($x_1 = x_s$).

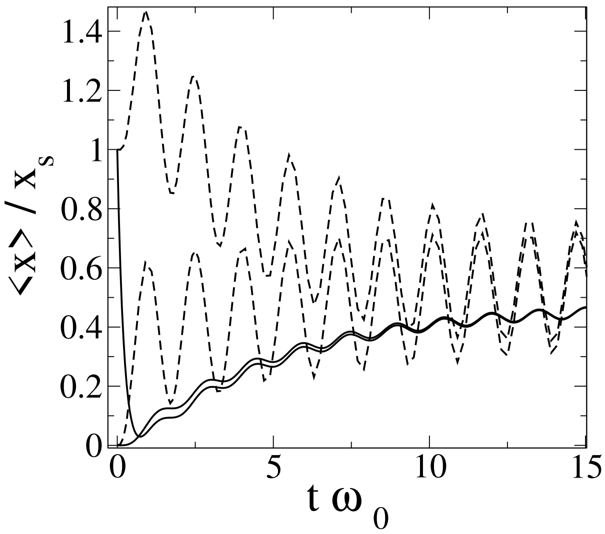

Figure 4.7: Evolution of the mean value of reaction coordinate x for initially unshifted ($x_1 = 0$) and shifted ($x_1 = x_s$) wave packets: results of Eq. (4.69) (solid lines) and Redfield results within Markov approximation (dashed lines). $x_s = 0.1x_0, \gamma = 5\omega_0$, the other parameters are the same as in Fig. 4.2.

perturbation into account it will be possible to consider a variety of electron transfer configurations, initial conditions, and temperatures. These results can then be compared with existing exact results (e.g. [20, 28]).

Next, the results for an intermediate system-bath coupling are shown in Figs. 4.5 and 4.6 for initially unshifted and shifted Gaussian wave packets. Here we compare the results of our perturbation theory with the results given by the Redfield method within and beyond the Markov approximation. The extended Redfield theory beyond the Markov approximation is similar to that described in Ref. [27] but its implementation is based on a numerical decomposition of the spectral density similar to that in Ref. [63]. Details are given in [43]. It is known that for stronger damping Redfield theory does not give satisfactory results, but we still have occasionally good correspondence between the Redfield results and the results obtained within the present perturbative treatment. For the case of an unshifted initial wave packet the standard Markovian and the extended non-Markovian Redfield theory are quite similar. The non-Markovian theory seems to perform even a little worse which might be connected to small errors introduced by fitting the spectral density. The behavior is quite different for a shifted initial Gaussian wave packet already at short times. There are some memory effects which can be equally well described by the present perturbative treatment in the shift as well as by the non-Markovian extension of the Redfield theory.

Finally, Fig. 4.7 shows the results for the overdamped case. Comparing the solid curves for initially shifted and unshifted wave packets one can see an initial fast transfer of the wave packet to the left potential surface for times $t\omega_0 \leq 1$ which is described by the first term of Eq. (4.69). This fast relaxation of the vibrational mode in case of the initially shifted wave packet occurs while the electronic subsystem in fact stays in the first electronic state $|1\rangle$. Then the reaction coordinate is driven by the undamped electronic subsystem from one side, and by the bath from the other. Thus the mean value of x goes to the point in the middle between the minima of the potential surfaces approaching thermal equilibrium, slightly oscillating with the Rabi frequency. For $t\omega_0 > 1$ the electron transfer dynamics of the shifted and unshifted wave packets described by the second term of Eq. (4.69) are very similar. The Redfield theory gives incorrect results in this case as it is expected but the frequency of the oscillations corresponding to the transition between the electronic states is the same for the present perturbative method and for the Redfield theory.

4.7 Summary

In this chapter we developed an approach to dissipative curve-crossing vibrational dynamics based on the path integral representation of the reduced density matrix for the reaction coordinate. The presented method has no restriction to weak system-bath interaction like the Redfield theory [7, 60, 76] nor to weak intercenter coupling [55], but the coordinate shift between the potential energy surfaces is assumed to be small (Eq. (4.54)). The mapping approach [84, 89, 95] was used for the formulation of the Lagrangian of the electronic system and the path integral in a combined phase-space and coherent-state representation was evaluated for the determination of the evolution operator. Eliminating the bath and applying the stationary phase method to the vibrational trajectories we got a non-Gaussian coherent-state path integral over the electronic trajectories which can be calculated perturbatively with the help of the generating functional. As a result, the dynamics of a Gaussian wave packet in first order of the present perturbation theory in case of factorized initial system-bath conditions has been considered. Also we investigated the validity range of the present treatment by comparing with the results given by the Redfield method in case of weak system-bath coupling. It was found that our perturbation theory works properly at short times but has deviations from the correct dynamics approaching thermal equilibrium ($t \to \infty$) when the terms of higher orders of the perturbation become important. Besides, in the overdamped case the vibrational dynamics in one potential energy surface turns out to be very similar to the dynamics of the electron transfer between the potential surfaces weakly shifted in the coordinate x.

In principle, non-Gaussian path integrals frequently appear in the path integral formulation of the dynamics of coupled systems. One of the general ways of calculating such integrals is the so-called variational perturbation theory [45] which gives a possibility of calculating non-Gaussian path integrals without a restriction to a small non-Gaussian part and which is based on the same perturbation theory as employed above. A similar method of renormalizing system parameters was used in [86,87] based on the small polaron transformation (see, for example, [74]). It requires the optimization of a large number of variational parameters for the system and the system-bath coupling parameters. In our path integral formulation the bath is eliminated and only few variational parameters have to be optimized. In the next chapter we will develop an approach to the population dynamics in the curve-crossing system based on the treatment described in this chapter with the implementation of the variational perturbation theory.

Chapter 5

Dissipative population dynamics and decoherence rate

In this section we will consider the population dynamics of the electronic states in the dissipative curve-crossing system described by the Hamiltonian (4.3). This is the case of population dynamics in two-center electron transfer systems. Here we will use the path integral formulation of the problem based on the non-Gaussian path integrals developed in the previous section. We construct the perturbation theory in the small coordinate shift between the potential energy surfaces and then consider the leading terms of the perturbative expansion for the population dynamics. Those terms appear to be of the next (second) order in the expansion parameter x_s/x_0 Eq. (4.54) while the leading term for the vibrational dynamics is of first order. The perturbative approach which will be developed in this chapter is a perturbation theory for the description of the transition between discrete quantum levels. It is known that the lowest orders of such a kind of time-dependent perturbation theories in most cases give results which are valid only at the beginning of the time evolution of the system, i.e. in the time-domains which are smaller than characteristic transition times in the systems. One of the first treatments for the description of the evolution of a system in the large time domains was the Weisskopf-Wigner method [104,105] which is heuristic and is not based on a consecutive perturbative expansion in some small parameter. One of the more consistent and powerful methods is the perturbation theory for the operator of the resolvent [11]. The main problem of obtaining the time evolution of the system at large times within the time-dependent perturbation theory is connected with the fact that the perturbation brings some contribution to the phase of the oscillations in the system and that with growing time the phase increases to infinity. Directly expanding the result in some small parameter, one obtains the so-called secular terms in this expansion which have a power-law dependence on time. Thus, this form of perturbation expansion fails to work when the time is large. The Poincare-Lindstedt method [8, 69] helps to avoid the appearance of secular terms in the perturbative expansion by taking into account that the frequency of the system oscillations can also be expanded in the parameter of the perturbation theory. In this way one gets a perturbative expansion for the frequency as well as for the whole result. This treatment was successfully applied to some problems of nonlinear dynamics, for example, the anharmonic oscillator [72].

The method of generating functional employed in the previous chapter for the perturbative expansion cannot be used for higher orders of our perturbation theory since already in second order in the small coordinate shift one gets secular terms. Here we will obtain the perturbative expansion for the frequency of the Rabi oscillations in the two-level system by using a specific form of the expansion for the stationary electronic trajectories while the electronic-vibrational interaction is assumed to be small. The influence of the bath leads to the appearance of an imaginary part in the leading term of the perturbative expansion for the Rabi frequency, and this part describes the damping of the Rabi oscillations.

Our next step is to apply the variational perturbation theory [45] to the expansion for the frequency. The variational perturbation theory is based on a variational approach of Feynman and Kleinert [29] and, in contrast to the ordinary perturbation theory, provides an approximate method to get convergent expansions. In many cases this treatment allows to calculate otherwise unsolvable (non-Gaussian) path integrals. Having the ordinary perturbation expansion which is valid only for small values of the expansion parameter, we can variationally optimize this result and then obtain the expansion valid in case of large parameters of the perturbation theory. This procedure of resummation of the weak-coupling series and reproducing the strong-coupling result was applied to the frequency of the classical anharmonic oscillator [72]. In addition, the variational perturbation theory was successfully applied to many problems of quantum statistics [1,50], Markov processes [46] and soft matter [2,3]. Finally, we obtain an optimized value of the decoherence rate in the population dynamics for the curve-crossing problem.

5.1 General formulation. Forward and backward electronic path integrals

In this section we will give the general expression for the population of the electronic states in the curve-crossing system. First, the electronic path integral is calculated and in this way the perturbation theory in a small electronic-vibronic coupling is constructed. As a result one eliminates the electronic subsystem and gets the electronic population as the path integral over the vibrational trajectories.

5.1.1 Electronic path integrals as functionals of the vibronic trajectories

Below we will, as in the previous chapter, consider the relevant system prepared initially in a state which is described by a density matrix of the form (4.19), i.e. the electronic subsystem is initially in state $|1\rangle$ while the wave function of the vibronic subsystem is represented by a Gaussian wave packet (3.97). In our calculations we will concentrate on the time evolution of the population of the first electronic state. So our purpose is to calculate the matrix element of the reduced density matrix of the electronic subsystem

$$P_1(t) = \langle 1|\mathrm{Tr}_v \mathrm{Tr}_b \rho(t)|1\rangle \ . \tag{5.1}$$

Using the path integral formulation derived in Secs. 4.2 and 4.3 we can write the population P_1 in the form of the functional integral

$$\begin{aligned} P_1(t) &= \int dx dx_i dx_i' \psi_0(x_i)\psi_0(x_i') \int_{x(0)=x_i}^{x(t)=x} D[x(\tau)] \int_{x'(0)=x_i'}^{x'(t)=x} D[x'(\tau)] \Upsilon[x(\tau), x'(\tau)] \\ &\quad \times \exp\left(iS_0[x(\tau)] - iS_0[x'(\tau)] - S_{inf}[x(\tau), x'(\tau)]\right) \ , \end{aligned} \tag{5.2}$$

where the functional Υ reads

$$\begin{aligned} \Upsilon[x(\tau), x'(\tau)] &= \prod_{\alpha=1}^{4}\prod_{i=1}^{2}\int \frac{da_{i\alpha}da_{i\alpha}^*}{\pi} a_{11}a_{12}^*a_{13}a_{14}^* \exp\left(-\sum_{n=1}^{2}\sum_{\beta=1}^{4}|a_{n\beta}|^2\right) \\ &\quad \times \int D[\{a_n(\tau)\},\{a_n^*(\tau)\}] D[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}] \\ &\quad \times \exp\Big(S_{el}[\{a_n(\tau)\},\{a_n^*(\tau)\}] + \tilde S_{el}[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}] \\ &\quad + iS_{v-el}[x(\tau), x'(\tau), a_2(\tau), a_2^*(\tau), \tilde a_2(\tau), \tilde a_2^*(\tau)]\Big) \ . \end{aligned} \tag{5.3}$$

Here the actions S_{inf} , S_0 , $S_{el}, \tilde S_{el}$ are determined by Eqs. (2.38, 4.24) and (4.12, 4.17), respectively. Also for the integration over the end points of the electronic trajectories in the expression for the functional Υ the definition (3.1) has been used. Then, the functional Υ can be split into the product of two functionals $\mathcal{W}$ and $\tilde{\mathcal{W}}$

$$\Upsilon[x(\tau), x'(\tau)] = \mathcal{W}[x(\tau)]\tilde{\mathcal{W}}[x'(\tau)] \ , \tag{5.4}$$

which correspond to the forward and backward electronic path integrals, respectively, and are determined as

$$\mathcal{W}[x(\tau)] = \prod_{i=1}^{2}\int \frac{da_i da_i^*}{\pi}\int \frac{da_i' da_i'^*}{\pi} a_1 a_1'^* \exp\left[-\sum_{n=1}^{2}\left(|a_n|^2 + |a_n'|^2\right)\right] \tag{5.5}$$

$$\times \int D[\{a_n(\tau)\},\{a_n^*(\tau)\}] \exp\left(S_{el}[\{a_n(\tau)\},\{a_n^*(\tau)\}] + i\int_0^t d\tau \frac{\omega_0 x_s}{x_0^2} x(\tau) a_2^*(\tau) a_2(\tau)\right) \ ,$$

and

$$\tilde{\mathcal{W}}[x'(\tau)] = \prod_{i=1}^{2}\int \frac{d\tilde a_i d\tilde a_i^*}{\pi}\int \frac{d\tilde a_i' d\tilde a_i'^*}{\pi} \tilde a_1 \tilde a_1'^* \exp\left[-\sum_{n=1}^{2}\left(|\tilde a_n|^2 + |\tilde a_n'|^2\right)\right] \tag{5.6}$$

$$\times \int D[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}] \exp\left(\tilde S_{el}[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}] - i\int_0^t d\tau \frac{\omega_0 x_s}{x_0^2} x'(\tau) \tilde a_2^*(\tau) \tilde a_2(\tau)\right) \ .$$

For our purposes it is convenient to use the action $\tilde S_{el}$ for the backward path integral on the right hand side of Eq. (5.6) in the form

$$\tilde S_{el}[\{\tilde a_n(\tau)\},\{\tilde a_n^*(\tau)\}] = \tilde a_1^*(t)\tilde a_1(t) + \tilde a_2^*(t)\tilde a_2(t) - \int_0^t d\tau \tilde{\mathcal{L}}_{el}(\tau) \tag{5.7}$$

with the Lagrangian function

$$\tilde{\mathcal{L}}_{el}(\tau) = \dot{\tilde{a}}_1^*(\tau)\tilde{a}_1(\tau) + \dot{\tilde{a}}_2^*(\tau)\tilde{a}_2(\tau) - i\epsilon\tilde{a}_2^*(\tau)\tilde{a}_2(\tau) - i\Delta(\tilde{a}_1^*(\tau)\tilde{a}_2(\tau) + \tilde{a}_2^*(\tau)\tilde{a}_1(\tau)) \ , \quad (5.8)$$

which can be obtained from the action (4.17) by integration by parts of the terms with time derivatives. The electronic action S_{el} in the forward path integral $\mathcal{W}$ (5.5) remains the same as in Eq. (4.12).

So we determined the electronic forward and backward path integrals as functionals of the vibronic trajectories. Those integrals are of Gaussian type and our aim is to evaluate them with the help of the stationary phase method. First, let us consider the forward path integral $\mathcal{W}$. Using the standard condition for the extremum of the action

$$\delta\left(S_{el}[\{a_n(\tau)\},\{a_n^*(\tau)\}] + i\int_0^t d\tau \frac{\omega_0 x_s}{x_0^2} x(\tau)a_2^*(\tau)a_2(\tau)\right) = 0 \quad (5.9)$$

one gets the equations for the stationary electronic trajectories (the stationary trajectories are marked by a bar)

$$\dot{\bar{a}}_1(s) + i\Delta\bar{a}_2(s) = 0 \ , \quad (5.10)$$

$$\dot{\bar{a}}_2(s) + i\epsilon\bar{a}_2(s) + i\Delta\bar{a}_1(s) - i\frac{\omega_0 x_s}{x_0^2}x(s)\bar{a}_2(s) = 0 \ , \quad (5.11)$$

$$\dot{\bar{a}}_1^*(s) - i\Delta\bar{a}_2^*(s) = 0 \ , \quad (5.12)$$

$$\dot{\bar{a}}_2^*(s) - i\epsilon\bar{a}_2^*(s) - i\Delta\bar{a}_1^*(s) + i\frac{\omega_0 x_s}{x_0^2}x(s)\bar{a}_2^*(s) = 0 \ , \quad (5.13)$$

which must be solved with the boundary conditions

$$\bar{a}_1^*(t) = a_1^* \ , \qquad \bar{a}_2^*(t) = a_2^* \ , \quad (5.14)$$

$$\bar{a}_1(0) = a_1' \ , \qquad \bar{a}_2(0) = a_2' \ . \quad (5.15)$$

The integral over the deviations from the stationary trajectories equals unity since the trajectories presenting the deviations have zero end points. Hence the result of the integration over all paths in Eq. (5.5) is given by

$$\int D[\{a_n(\tau)\},\{a_n^*(\tau)\}] \exp\left(S_{el}[\{a_n(\tau)\},\{a_n^*(\tau)\}] + i\int_0^t d\tau \frac{\omega_0 x_s}{x_0^2} x(\tau)a_2^*(\tau)a_2(\tau)\right)$$
$$= \exp\left(S_{el}[\{\bar{a}_n(\tau)\},\{\bar{a}_n^*(\tau)\}] + i\int_0^t d\tau \frac{\omega_0 x_s}{x_0^2} x(\tau)\bar{a}_2^*(\tau)\bar{a}_2(\tau)\right) \ . \quad (5.16)$$

The exponential factor here is evaluated on the stationary trajectories. Besides, employing the equations (5.10-5.13) one finds that the Lagrangian function corresponding to the full action in (5.5) is zero on the stationary trajectories, and it is left to evaluate only the terms depending on end points in the expression for S_{el}, i.e.

$$S_{el}[\{\bar{a}_n(\tau)\},\{\bar{a}_n^*(\tau)\}] = \bar{a}_1^*(t)\bar{a}_1(t) + \bar{a}_2^*(t)\bar{a}_2(t) = a_1^*\bar{a}_1(t) + a_2^*\bar{a}_2(t) \ . \quad (5.17)$$

Hence we have to solve only the first pair of equations for the stationary trajectories, i.e. Eqs. (5.10) and (5.11) in order to find the values $\bar{a}_1(t)$ and $\bar{a}_2(t)$.

5.1.2 Perturbative expansion for the stationary electronic trajectories

Let us rewrite Eqs. (5.10, 5.11) in the form

$$\bar{a}_2(s) = \frac{i}{\Delta}\dot{\bar{a}}_1(s) \;, \tag{5.18}$$

$$\ddot{\bar{a}}_1(s) + i\epsilon\dot{\bar{a}}_1(s) + \Delta^2\bar{a}_1(s) - i\frac{\omega_0 x_s}{x_0^2}x(s)\dot{\bar{a}}_1(s) = 0 \;. \tag{5.19}$$

Since we have an arbitrary function of time $x(s)$ in the last term on the left hand side of Eq. (5.19), this system of equations is not solvable exactly. We will try to find the expansion of the solution in powers of the small parameter x_s/x_0 and here we will restrict ourselves to the first order of the perturbation. Next, we have to prevent the appearance of secular terms in the perturbative expansion of the full result for the population $P_1(t)$. It is clear that the standard method of obtaining the perturbative expansion in the form $\bar{a}_1(s) = \bar{a}_1^{(0)}(s) + (x_s/x_0)\bar{a}_1^{(1)}(s) + ...$ is not suitable here. For instance, it is easy to see that in case of $x(s) = const$ one gets a secular term in the first order perturbation term. In order to construct the correct perturbative expansion one has to note that the perturbation brings some contribution to the phase of the solution $\bar{a}_1(s)$. Thus, the more appropriate procedure is to find the perturbative expansion not for the solution $\bar{a}(s)$ but for some another function of time associated with the phase. Supposing that the function $x(s)$ is a finite function of time s, let us try to find the solution in the following form

$$\bar{a}_1(s) = e^{\lambda(s)} \;. \tag{5.20}$$

Substituting this expression into Eq. (5.19) one gets the equation for the function $\lambda(s)$

$$\ddot{\lambda}(s) + \dot{\lambda}^2(s) + i\epsilon\dot{\lambda}(s) + \Delta^2 - i\frac{\omega_0 x_s}{x_0^2}x(s)\dot{\lambda}(s) = 0 \tag{5.21}$$

which will be solved perturbatively, i.e.

$$\lambda(s) = \lambda^{(0)}(s) + \lambda^{(1)}(s) \;, \tag{5.22}$$

where $\lambda^{(1)}(s)$ is of the order of x_s/x_0. Thus, the zeroth order solution is given by

$$\lambda_{1,2}^{(0)}(s) = -i\Omega_{1,2}s \;, \qquad \Omega_{1,2} = \frac{\epsilon \mp h}{2} \tag{5.23}$$

and describes the pure Rabi oscillations with the frequency $h = \Omega_2 - \Omega_1 = -\sqrt{\epsilon^2 + (2\Delta)^2}$ without the influence of the vibrational mode. Then, taking only the terms of the first order of x_s/x_0 one gets the equation for the first expansion term

$$\ddot{\lambda}_{1,2}^{(1)}(s) + i(\epsilon - 2\Omega_{1,2})\dot{\lambda}_{1,2}^{(1)}(s) - \frac{\omega_0 x_s}{x_0^2}\Omega_{1,2}x(s) = 0 \;. \tag{5.24}$$

Only the solution of zeroth order satisfies the initial conditions for the trajectories (5.15) while the perturbative terms have zero end point. Hence equation (5.24) has to be solved starting from

$$\lambda_{1,2}^{(1)}(0) = \dot{\lambda}_{1,2}^{(1)}(0) = 0 \ . \tag{5.25}$$

Thus, the solution is given by

$$\lambda_{1,2}^{(1)}(s) = Q_0 \Omega_{1,2} \int_0^s \int_0^{s'} ds' ds'' x(s'') \exp[-i(\epsilon - 2\Omega_{1,2})(s' - s'')] \ . \tag{5.26}$$

Finally, using the boundary conditions (5.15) one can give the solution of the system Eqs. (5.18, 5.19) in the form

$$\bar{a}_1(s) = \frac{a_1' \dot{\lambda}_2(0) + i\Delta a_2'}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} e^{\lambda_1(s)} - \frac{a_1' \dot{\lambda}_1(0) + i\Delta a_2'}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} e^{\lambda_2(s)} \ , \tag{5.27}$$

$$\bar{a}_2(s) = \frac{i}{\Delta} \left[\dot{\lambda}_1(s) \frac{a_1' \dot{\lambda}_2(0) + i\Delta a_2'}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} e^{\lambda_1(s)} - \dot{\lambda}_2(s) \frac{a_1' \dot{\lambda}_1(0) + i\Delta a_2'}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} e^{\lambda_2(s)} \right] \ . \tag{5.28}$$

Substituting the solutions for the stationary trajectories (5.27) and (5.28) at time t into the expression for the electronic action (5.17) one can write the following integral expression for the forward path integral $\mathcal{W}$

$$\begin{aligned} \mathcal{W}[x(\tau)] \ &= \ \prod_{i=1}^{2} \int \frac{da_i da_i^*}{\pi} \int \frac{da_i' da_i'^*}{\pi} a_1 a_1'^* \\ &\times \exp\left[-\sum_{n=1}^{2} \left(|a_n|^2 + |a_n'|^2 \right) + p_{11} a_1' a_1^* + p_{12} a_1' a_2^* + p_{21} a_2' a_1^* + p_{22} a_2' a_2^* \right] \ . \end{aligned} \tag{5.29}$$

The time-dependent coefficients $p_{ij}(t)$ are functionals of $x(s)$

$$p_{11}(t) = \frac{\dot{\lambda}_2(0) e^{\lambda_1(t)} - \dot{\lambda}_1(0) e^{\lambda_2(t)}}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} \ , \tag{5.30}$$

$$p_{12}(t) = \frac{i}{\Delta} \frac{\dot{\lambda}_2(0) \dot{\lambda}_1(t) e^{\lambda_1(t)} - \dot{\lambda}_1(0) \dot{\lambda}_2(t) e^{\lambda_2(t)}}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} \ , \tag{5.31}$$

$$p_{21}(t) = i\Delta \frac{e^{\lambda_1(t)} - e^{\lambda_2(t)}}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} \ , \tag{5.32}$$

$$p_{22}(t) = -\frac{\dot{\lambda}_1(t) e^{\lambda_1(t)} - \dot{\lambda}_2(t) e^{\lambda_2(t)}}{\dot{\lambda}_2(0) - \dot{\lambda}_1(0)} \ . \tag{5.33}$$

Here the perturbative expansion for $\lambda_{1,2}(s)$ is given by

$$\lambda_{1,2}(s) = \lambda_{1,2}[x(\tau)] = -i\Omega_{1,2}s \pm i\frac{\omega_0 x_s}{x_0^2}\frac{\Omega_{1,2}}{h}\int_0^s d\tau x(\tau)[e^{\mp ih(s-\tau)} - 1] \ , \qquad (5.34)$$

where the upper and lower signs correspond to the indices 1 and 2, respectively. Calculating the integrals over the end points of the stationary trajectories in (5.29) using the integral formula (3.80) we obtain the final result for the functional $\mathcal{W}$

$$\mathcal{W} = p_{11}(t) \ . \qquad (5.35)$$

Analogously, for the calculation of the backward path integral $\tilde{\mathcal{W}}$ (5.6) one has to evaluate the electronic action $\tilde{S}_{el}$ (5.7) on the stationary trajectories with the end points

$$\bar{\tilde{a}}_1(t) = \tilde{a}_1' \ , \qquad \bar{\tilde{a}}_2(t) = \tilde{a}_2' \ , \qquad (5.36)$$

$$\bar{\tilde{a}}_1^*(0) = \tilde{a}_1^* \ , \qquad \bar{\tilde{a}}_2^*(0) = \tilde{a}_2^* \ . \qquad (5.37)$$

Thus, the action on the stationary trajectories reads

$$\tilde{S}_{el} = \bar{\tilde{a}}_1^*(t)\bar{\tilde{a}}_1(t) + \bar{\tilde{a}}_2^*(t)\bar{\tilde{a}}_2(t) = \bar{\tilde{a}}_1^*(t)\tilde{a}_1 + \bar{\tilde{a}}_2^*(t)\tilde{a}_2 \ . \qquad (5.38)$$

Hence, one has to solve the equations only for the trajectories $\bar{\tilde{a}}_1^*(\tau)$ and $\bar{\tilde{a}}_2^*(\tau)$ which can be obtained from the condition for the extremum of the action

$$\dot{\bar{\tilde{a}}}_1^* = i\Delta\bar{\tilde{a}}_2^* \ , \qquad (5.39)$$

$$\dot{\bar{\tilde{a}}}_2^* = i\epsilon\bar{\tilde{a}}_2^* + i\Delta\bar{\tilde{a}}_1^* - i\frac{\omega_0 x_s}{x_0^2}x'(s)\bar{\tilde{a}}_2^* \ . \qquad (5.40)$$

These equations must be solved with the boundary conditions (5.37). Performing the expansion in the small parameter x_s/x_0 in the same manner as for the trajectories in the forward path integral, one can give the solution of the above equations in the form

$$\bar{\tilde{a}}_1^*(s) = \frac{\tilde{a}_1^*\dot{\tilde{\lambda}}_2^*(0) - i\Delta\tilde{a}_2^*}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)}e^{\tilde{\lambda}_1^*(s)} - \frac{\tilde{a}_1^*\dot{\tilde{\lambda}}_1^*(0) - i\Delta\tilde{a}_2^*}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)}e^{\tilde{\lambda}_2^*(s)} \ , \qquad (5.41)$$

$$\bar{\tilde{a}}_2(s) = -\frac{i}{\Delta}\left[\dot{\tilde{\lambda}}_1^*(s)\frac{\tilde{a}_1^*\dot{\tilde{\lambda}}_2^*(0) - i\Delta\tilde{a}_2^*}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)}e^{\tilde{\lambda}_1^*(s)} - \dot{\tilde{\lambda}}_2^*(s)\frac{\tilde{a}_1^*\dot{\tilde{\lambda}}_1^*(0) - i\Delta\tilde{a}_2^*}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)}e^{\tilde{\lambda}_2^*(s)}\right] \ . \qquad (5.42)$$

Substituting this solution into the expression for the action (5.38), one gets for the backward path integral

$$\begin{aligned}\tilde{\mathcal{W}}[x'(\tau)] \ &= \ \prod_{i=1}^{2}\int\frac{d\tilde{a}_i d\tilde{a}_i^*}{\pi}\int\frac{d\tilde{a}_i' d\tilde{a}_i'^*}{\pi}\tilde{a}_1\tilde{a}_1'^* \qquad (5.43)\\ &\times \exp\left[-\sum_{n=1}^{2}\left(|\tilde{a}_n|^2 + |\tilde{a}_n'|^2\right) + \tilde{p}_{11}\tilde{a}_1'\tilde{a}_1^* + \tilde{p}_{12}\tilde{a}_1'\tilde{a}_2^* + \tilde{p}_{21}\tilde{a}_2'\tilde{a}_1^* + \tilde{p}_{22}\tilde{a}_2'\tilde{a}_2^*\right]\end{aligned}$$

with the coefficients

$$\tilde{p}_{11}(t) = \frac{\dot{\tilde{\lambda}}_2^*(0) e^{\tilde{\lambda}_1^*(t)} - \dot{\tilde{\lambda}}_1^*(0) e^{\tilde{\lambda}_2^*(t)}}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)} \ , \tag{5.44}$$

$$\tilde{p}_{12}(t) = -\frac{i}{\Delta} \frac{\dot{\tilde{\lambda}}_2^*(0)\dot{\tilde{\lambda}}_1^*(t) e^{\tilde{\lambda}_1^*(t)} - \dot{\tilde{\lambda}}_1^*(0)\dot{\tilde{\lambda}}_2^*(t) e^{\tilde{\lambda}_2^*(t)}}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)} \ , \tag{5.45}$$

$$\tilde{p}_{21}(t) = -i\Delta \frac{e^{\tilde{\lambda}_1^*(t)} - e^{\tilde{\lambda}_2^*(t)}}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)} \ , \tag{5.46}$$

$$\tilde{p}_{22}(t) = -\frac{\dot{\tilde{\lambda}}_1^*(t) e^{\tilde{\lambda}_1^*(t)} - \dot{\tilde{\lambda}}_2^*(t) e^{\tilde{\lambda}_2^*(t)}}{\dot{\tilde{\lambda}}_2^*(0) - \dot{\tilde{\lambda}}_1^*(0)} \ . \tag{5.47}$$

The functional $\tilde{\lambda}(s)$ here is defined as

$$\tilde{\lambda}_{1,2}(s) = \lambda_{1,2}[x'(\tau)] \ . \tag{5.48}$$

Finally, after evaluation of the integral over the end points on the right hand side of Eq. (5.43) the functional $\tilde{\mathcal{W}}$ reads

$$\tilde{\mathcal{W}} = \tilde{p}_{11}(t) \ . \tag{5.49}$$

Now using Eqs. (5.35,5.49) and (5.4) we can give the functional of the vibrational trajectories Υ in the simple form

$$\Upsilon[x(\tau), x'(\tau)] = p_{11}[x(\tau)]\tilde{p}_{11}[x'(\tau)] \ . \tag{5.50}$$

5.2 Path integral for the reaction coordinate

In the previous section we eliminated the electronic subsystem from the functional integral expression (5.2) for the population of the first electronic state. The next task is to evaluate the remaining path integral describing the influence of the reaction coordinate x, i.e. the integral over the vibrational trajectories. The functional $\Upsilon[x(\tau), x'(\tau)]$ represents the influence of the electronic subsystem and has to be averaged over all trajectories of the reaction coordinate with the action of the pure dissipative vibrational mode $iS_0[x(\tau)] - iS_0[x'(\tau)] - S_{inf}[x(\tau), x'(\tau)]$.

First, let us calculate the functional Υ explicitly. We use the variables (4.26) for the vibrational trajectories. Using the expressions for the coefficients $p_{11}(t)$ and $\tilde{p}_{11}(t)$ (5.30,5.44) as well as the definition of the exponential factor λ (5.34), one gets for the functional Υ

$$\Upsilon[r(\tau), q(\tau)] = \frac{1}{h^2}\left[\Omega_2^2 e^{\mathcal{I}_1} + \Omega_1^2 e^{\mathcal{I}_2} - \Omega_1\Omega_2(e^{\mathcal{J}_1} + e^{\mathcal{J}_2})\right] \tag{5.51}$$

where

$$\mathcal{I}_1 = \lambda_1(t) + \tilde{\lambda}_1^*(t) = \frac{\omega_0 x_s}{x_0^2}\frac{\Omega_1}{h}\int_0^t ds[2r(s)\sin h(t-s) + iq(s)(\cos h(t-s) - 1)] \ , \quad (5.52)$$

$$\mathcal{I}_2 = \lambda_2(t) + \tilde{\lambda}_2^*(t) = \frac{\omega_0 x_s}{x_0^2}\frac{\Omega_2}{h}\int_0^t ds[2r(s)\sin h(t-s) - iq(s)(\cos h(t-s) - 1)] \ , \quad (5.53)$$

$$\mathcal{J}_1 = \lambda_1(t) + \tilde{\lambda}_2^*(t) = iht + i\frac{\omega_0 x_s}{x_0^2}\frac{1}{h}\int_0^t ds[\epsilon r(s) - q(s)h/2](e^{-ih(t-s)} - 1) \ , \quad (5.54)$$

$$\mathcal{J}_2 = \lambda_2(t) + \tilde{\lambda}_1^*(t) = -iht - i\frac{\omega_0 x_s}{x_0^2}\frac{1}{h}\int_0^t ds[\epsilon r(s) + q(s)h/2](e^{ih(t-s)} - 1) \ . \quad (5.55)$$

Now one has to average each of the exponents of the functionals $\mathcal{I}_{1,2}$ and $\mathcal{J}_{1,2}$. This functionals have linear dependences on the trajectories $r(\tau)$ and $q(\tau)$. At this point we have to recollect the vibronic generating functional Φ_0 (4.53) calculated in the Section (4.4). This functional was introduced as the averaged exponent of the functional of the electronic-vibronic interaction $\exp(iS_{v-el})$ (4.23), i.e.

$$\Phi_0[Q_-(s), Q_+(s)] = \left\langle \exp\left[i\int_0^t ds(r(s)Q_-(s) + q(s)Q_+(s))\right]\right\rangle \ , \quad (5.56)$$

where the averaging is performed over all paths of the dissipative vibrational mode with the action $iS_0[x(\tau)] - iS_0[x'(\tau)] - S_{inf}[x(\tau), x'(\tau)]$ - exactly as in the formula (5.2), and the functions $Q_-(s)$, $Q_+(s)$ are treated as auxiliary functions of time s. Then, we see that the action S_{v-el} and the functionals $\mathcal{I}_{1,2}$ and $\mathcal{J}_{1,2}$ have the same structure (linear dependence on vibronic trajectories). Hence one can use the vibronic generating functional (4.53) for the calculation of the population $P_1(t)$.

5.3 Decoherence rate

5.3.1 Ordinary perturbation theory

For the beginning, let us calculate the population P_1 in zeroth order which can be obtained from Eq. (5.2) by setting $x_s = 0$

$$\begin{aligned} P_1^{(0)} &= \Upsilon[r(\tau), q(\tau)]\Big|_{x_s=0} = \frac{1}{h^2}\left[\Omega_1^2 + \Omega_2^2 - \Omega_1\Omega_2(e^{iht} + e^{-iht})\right] \\ &= \frac{\epsilon^2 + h^2}{2h^2} + 2\frac{\Delta^2}{h^2}\cos ht \ . \end{aligned} \quad (5.57)$$

The latter expression presents pure Rabi oscillations of the population between two electronic states, and the amplitude of the oscillations is proportional to the squared intercenter coupling. In presence of dissipation the coherent oscillations described by the term $2\frac{\Delta^2}{h^2}\cos ht$ in Eq. (5.57) have to be damped. So it is reasonable to assume that the frequencies will have an imaginary part in case of non-zero coordinate shift x_s. These frequencies are determined by the functionals $\mathcal{J}_{1,2}$ in the expression for Υ in first order of the perturbation. In this way we will obtain the rate function which describes a loss of system phase. Actually, the damping process in the electronic subsystem is also characterized by one more rate function describing the process of the transfer of energy between system and bath via the reaction coordinate. In principle this function can be obtained by averaging the first two terms $\Omega_2^2 e^{\mathcal{I}_1} + \Omega_1^2 e^{\mathcal{I}_2}$ in Eq. (5.51).

Below we will focus on the calculation of the expansion for the frequency by averaging the term $e^{\mathcal{J}_1} + e^{\mathcal{J}_2}$ in Eq. (5.51) over all vibrational paths. As was written in the previous section, for this purpose one can use the expression for the vibronic generating functional $\Phi_0[Q_-(s), Q_+(s)] = \exp(\Lambda[Q_-(s), Q_+(s)])$ since the functionals $\mathcal{J}_{1,2}$ are linear in the trajectories $r(s)$ and $q(s)$. Instead of the functions $Q_-(s)$ and $Q_+(s)$ on the right hand side of Eq. (5.56) the corresponding functions from the functionals $\mathcal{J}_{1,2}$ must be taken. For instance, let us first consider the exponent $e^{\mathcal{J}_1}$

$$\langle e^{\mathcal{J}_1} \rangle = e^{\bar{\mathcal{J}}_1} \ . \tag{5.58}$$

Here the averaged functional $\bar{\mathcal{J}}_1$ is given by

$$\begin{aligned} \bar{\mathcal{J}}_1(t) &= \Lambda[Q'_-(s), Q'_+(s)] \ , \\ Q'_-(s) &= \frac{\omega_0 x_s}{x_0} \frac{\epsilon}{h} \left(e^{-ih(t-s)} - 1 \right) \ , \\ Q'_+(s) &= -\frac{1}{2} \frac{\omega_0 x_s}{x_0} \left(e^{-ih(t-s)} - 1 \right) \ . \end{aligned} \tag{5.59}$$

Evaluation of the function $\Lambda[Q'_-(s), Q'_+(s)]$ Eq. (4.50) gives terms of two types: finite functions of time and the functions which increase with increasing time. The former terms are small and can be neglected while the latter become important with growing time, i.e. we are interested in the long-time asymptotic behaviour of $\bar{\mathcal{J}}_1$. Thus, our aim is to extract the secular terms from the expression for the function $iht + \Lambda[Q'_-(s), Q'_+(s)]$ which will be denoted by $w(t)$. As in the previous chapter, here we will use the spectral density of Ohmic form with the infinite cut-off frequency, Eq. (3.75). The second term on the right hand side of Eq. (4.50) gives the imaginary secular term $-i\frac{\omega_0 \epsilon}{2h}\left(\frac{x_s}{x_0}\right)^2 t$. So we have

$$w(t) = iht - i\frac{\omega_0 \epsilon}{2h}\left(\frac{x_s}{x_0}\right)^2 t + \mathrm{Re}(w(t)) \ . \tag{5.60}$$

The real part of the secular term which is responsible for a damping can be extracted from the last integral in Eq. (4.51). The function $\xi(\tau)$ (4.29) in case of Ohmic dissipation (3.75) reads

$$\xi(\tau) = \frac{M\gamma}{\pi} \int_0^\infty \omega \cos(\omega\tau) \coth\left(\frac{\omega}{2T_b}\right) d\omega \ . \tag{5.61}$$

Calculating the integrals over time in the last term of the expression (4.51) one obtains that in general the terms growing in time can be given by the following integral over the frequencies of bath modes

$$\mathrm{Re}(w(t)) = \frac{\gamma\omega_0}{\pi}\left(\frac{\epsilon}{h}\right)^2\left(\frac{x_s}{x_0}\right)^2\int_0^\infty \coth\left(\frac{\omega}{2T_b}\right)\mathrm{Re}\left(\frac{e^{i\omega t}}{\omega_0^2-\omega^2+i\gamma\omega}\right)\frac{d\omega}{\omega}\,. \tag{5.62}$$

The latter integral is evaluable analytically in two limiting cases: low and high temperatures of the bath. The domain $(0, 2\omega_0+\gamma)$ brings the main contribution to the result of the integration (5.62). Thus, in the high temperature limit $T_b \gg \omega_0, \gamma$ one gets $\coth\frac{\omega}{2T_b} \approx \frac{2T_b}{\omega}$. So the integrand in Eq. (5.62) has a pole of second order at the point $\omega = 0$ which leads to the appearance of the time-linear term in $\mathrm{Re}(w(t))$. Evaluating the long-time asymptotic in Eq. (5.62), we can write the following expression for the secular term

$$w(t) = iht - i\frac{\omega_0\epsilon}{2h}\left(\frac{x_s}{x_0}\right)^2 t - \frac{\gamma T_b}{\omega_0}\left(\frac{\epsilon}{h}\right)^2\left(\frac{x_s}{x_0}\right)^2 t. \tag{5.63}$$

In the opposite case of low temperatures $T_b \ll \omega_0, \gamma$ $(\cosh\frac{\omega}{2T_b} \approx 1)$ the integrand in (5.62) has a pole of first order at $\omega = 0$ with gives a logarithmic dependence in time in the long-time asymptotic, i.e.

$$w(t) = iht - i\frac{\omega_0\epsilon}{2h}\left(\frac{x_s}{x_0}\right)^2 t - \frac{\gamma}{\omega_0}\left(\frac{\epsilon}{h}\right)^2\left(\frac{x_s}{x_0}\right)^2 \log(\omega_0 t). \tag{5.64}$$

Analogously with $\bar{\mathcal{J}}_1(t)$ one finds for the secular terms in $\bar{\mathcal{J}}_2(t)$ that $\bar{\mathcal{J}}_2(t) = w^*(t)$. Finally, instead of the factor $2\cos(ht)$ in the expression for the Rabi oscillations (5.57) we get the factor $e^{\bar{\mathcal{J}}_1(t)} + e^{\bar{\mathcal{J}}_2(t)} = e^{w(t)} + e^{w^*(t)}$ in presence of dissipation. The damping of the Rabi oscillations in the electronic subsystem is completely different for the regimes of high and low temperatures of the bath. In the former case the coherence is damped exponentially, i.e.

$$\begin{aligned} e^{w(t)} + e^{w^*(t)} &= 2\cos(h't)\exp\left[-\frac{\gamma T_b}{\omega_0}\left(\frac{\epsilon}{h}\right)^2\left(\frac{x_s}{x_0}\right)^2 t\right], \\ h' &= h - \frac{\omega_0\epsilon}{2h}\left(\frac{x_s}{x_0}\right)^2, \end{aligned} \tag{5.65}$$

while in the latter we get a power-law behaviour

$$e^{w(t)} + e^{w^*(t)} = 2\cos(h't)(\omega_0 t)^{-\frac{\gamma}{\omega_0}\left(\frac{\epsilon}{h}\right)^2\left(\frac{x_s}{x_0}\right)^2}. \tag{5.66}$$

The forms of damping (5.65) and (5.66) have been found for the analytically solvable model of the unbiased ($\Delta G_0 = 0$) dissipative two-level system in which the Hamiltonian of the system-bath interaction has an off-diagonal form in the states of the relevant system [21]. The high-temperature behaviour (5.65) can also be confirmed by the results of the Redfield theory in the case of weak system-bath coupling while the low temperature behaviour can be correctly described by the non-Markovian master equation [43]. Below we will consider the high temperature limit (5.63). The function $w(t)$ (5.63) can be treated as a perturbation expansion for the phase of the oscillations $w(t) = ut$ with the complex frequency

$$u = ih - iE_r \frac{\epsilon}{h} - 2E_r \frac{\gamma T}{\omega_0^2} \left(\frac{\epsilon}{h}\right)^2 , \tag{5.67}$$
$$\epsilon = E_r - \Delta G_0 , \qquad E_r = \frac{\omega_0}{2} \left(\frac{x_s}{x_0}\right)^2 ,$$

where the real part of u represents the damping rate. In the next section we will treat the perturbation expansion for u by means of the variational perturbation theory in order to get the expression for the damping rate $\mathrm{Re}(u)$ valid not only for small parameter x_s/x_0.

5.3.2 Application of the variational perturbation theory

Since the validity range of the expansion (5.67) for u is restricted to the small coordinate shift x_s, it diverges with increasing parameter x_s/x_0. The variational perturbation theory is a tool which turns the divergent perturbative expansion into a convergent one. Here we follow the standard treatment derived, for example, in Ref. [45]. The basic idea of this approach consists of introducing so-called variational parameters into the unperturbed system in order to approximate the real potential (including interaction) as well as possible for an arbitrary coupling. As the pure electronic subsystem is described by the energy shift ϵ and by the intercenter coupling Δ, let us choose both of them as variational parameters which will be denoted by $\tilde{\epsilon}$ and $\tilde{\Delta}$. We have to replace the original parameters ϵ and Δ in the Hamiltonian of the pure electronic subsystem

$$\epsilon = \tilde{\epsilon} + (\epsilon - \tilde{\epsilon}) , \qquad \Delta = \tilde{\Delta} + (\Delta - \tilde{\Delta}) , \tag{5.68}$$

$$H_{el} = \tilde{\epsilon}|2\rangle\langle 2| + \tilde{\Delta}(|1\rangle\langle 2| + |2\rangle\langle 1|) + (\epsilon - \tilde{\epsilon})|2\rangle\langle 2| + (\Delta - \tilde{\Delta})(|1\rangle\langle 2| + |2\rangle\langle 1|) . \tag{5.69}$$

The last two terms on the right hand side of the expression (5.69) will be treated as a perturbation, and the differences $\epsilon - \tilde{\epsilon}$ and $\Delta - \tilde{\Delta}$ are assumed to be of the order of $(x_s/x_0)^2$. Hence, we have to replace ϵ and Δ by $\tilde{\epsilon}$ and $\tilde{\Delta}$ in the expansion (5.67) and then reexpand each term with respect to small $\epsilon - \tilde{\epsilon}$ and $\Delta - \tilde{\Delta}$ leaving only the terms of the zeroth and first order in $(x_s/x_0)^2$. The reexpanded frequency will be denoted by $\tilde{u}$

$$\tilde{u} = i\tilde{h} - iE_r \frac{\tilde{\epsilon}}{\tilde{h}} - 2E_r \frac{\gamma T_b}{\omega_0^2} \left(\frac{\tilde{\epsilon}}{\tilde{h}}\right)^2 + i\frac{\partial \tilde{h}}{\partial \tilde{\epsilon}}(\epsilon - \tilde{\epsilon}) + i\frac{\partial \tilde{h}}{\partial \tilde{\Delta}}(\Delta - \tilde{\Delta}) , \tag{5.70}$$

where $\tilde{h} = h(\tilde{\epsilon}, \tilde{\Delta})$. Now let us suppose that we are able to calculate all perturbative terms of all orders in x_s/x_0 in the expansion for $\tilde{u}$. It is clear that in this case the final result does not depend on the variational parameters. Hence, the optimal values of the parameters $\tilde{\epsilon}$ and $\tilde{\Delta}$ for the truncated perturbative expansion can be found from the conditions of minimal influence of them on the final result (so-called principle of minimal sensitivity)

$$\frac{\partial \tilde{u}}{\partial \tilde{\epsilon}} = 0 , \qquad \frac{\partial \tilde{u}}{\partial \tilde{\Delta}} = 0 . \tag{5.71}$$

Using expansion (5.70) one gets the equation for the optimal variational parameters

$$\epsilon - \tilde{\epsilon} = E_r + (\Delta - \tilde{\Delta})\frac{\tilde{\epsilon}}{\tilde{\Delta}} - 4iE_r\frac{\gamma T_b}{\omega_0^2}\frac{\tilde{\epsilon}}{\tilde{h}} , \tag{5.72}$$

$$\Delta - \tilde{\Delta} = -E_r\frac{\tilde{\Delta}}{\tilde{\epsilon}} + (\epsilon - \tilde{\epsilon})\frac{\tilde{\Delta}}{\tilde{\epsilon}} + 4iE_r\frac{\gamma T_b}{\omega_0^2}\frac{\tilde{\Delta}}{\tilde{h}} . \tag{5.73}$$

One can see that Eqs. (5.72) and (5.73) are identical (express, for instance, $\Delta - \tilde{\Delta}$ from (5.73) and substitute into (5.72)). Hence, we can use one of these equations (for example, Eq. (5.72)) with some additional conditions. Let us split Eq. (5.72) into two equations

$$\tilde{\epsilon} = \epsilon - E_r = -\Delta G_0 , \tag{5.74}$$

$$\Delta - \tilde{\Delta} = 4iE_r\frac{\gamma T_b}{\omega_0^2}\frac{\tilde{\Delta}}{\tilde{h}} . \tag{5.75}$$

Now the optimized value of the Rabi frequency $\tilde{h}$ depends on the original energy shift ΔG_0 due to Eq. (5.74). The equation for the optimized frequency $\tilde{u}$ then reads

$$\tilde{u} = i\tilde{h} - 2E_r\frac{\gamma T_b}{\omega_0^2}\left[1 + 4\left(\frac{\tilde{\Delta}}{\tilde{h}}\right)^2\right] , \tag{5.76}$$

where $\tilde{h} = -\sqrt{(\Delta G_0)^2 + (2\tilde{\Delta})^2}$. The optimal value of the decoherence rate $D = \mathrm{Re}(\tilde{u})$ can be obtained substituting the solution of the equation for the variational parameter $\tilde{\Delta}$ (5.75) into Eq. (5.76). The results for the rate D as function of the coordinate shift x_s are shown in Fig. 5.1 for three different values of the dissipation constant γ.

The dependence of D on x_s has a square form if x_s is small enough and the ordinary perturbation expansion (5.67) is valid. After some value of x_s (peak position of each curve on Fig. (5.1)) the damping rate decreases with increasing x_s. In order to understand this behaviour we have to analyze the Hamiltonians of the electronic-vibronic coupling and system-bath interaction

$$H_{v-el} + H_i = -\omega_0\frac{x_s x}{x_0^2}|2\rangle\langle 2| - x\sum_{\omega} c_\omega x_\omega . \tag{5.77}$$

Both terms on the right hand side of this expression have a linear dependence on the coordinate x. Increasing the parameter x_s leads to an increase of the influence of H_{v-el} in comparison to H_i. Thus, if x_s is large enough, the system-bath coupling becomes small with respect to the relevant system Hamiltonian. Hence, the damping in the relevant system becomes weak for large values of x_s.

On the other hand the damping rate decreases with increasing coupling constant γ if the coordinate shift is large. The possible explanation of this fact is that the mean value of the coordinate x in the electronic-vibronic interaction Hamiltonian rapidly goes

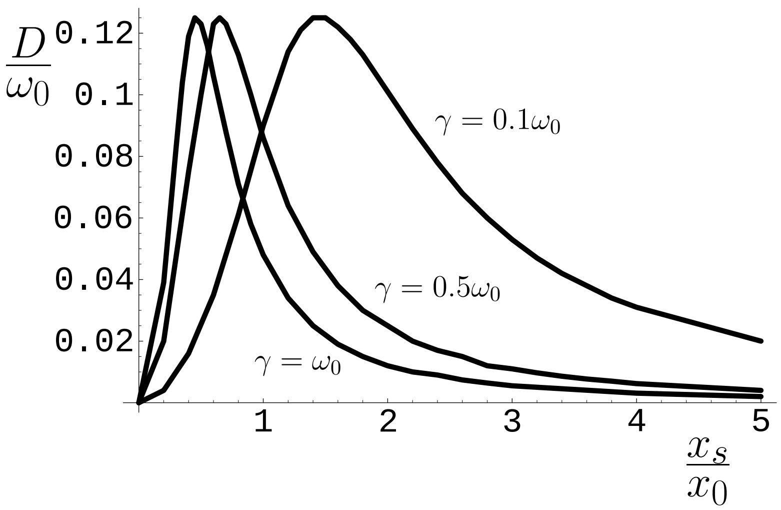

Figure 5.1: Decoherence rate $D = \mathrm{Re}(\tilde{u})$ as the function of the expansion parameter x_s/x_0 for dissipation constants $\gamma = 0.1\omega_0, 0.5\omega_0, \omega_0$, $T_b = 5\omega_0, \Delta G_0 = \Delta = \omega_0$.

to the equilibrium position like $\bar{x}(t) = x_s - x_s \cos(\Omega_0 t) e^{-\gamma t/2}$ for the electronic state $|2\rangle$ and $\bar{x}(t) = x_s \cos(\Omega_0 t) e^{-\gamma t/2}$ for the electronic state $|1\rangle$ if the electronic subsystem stays in one of the electronic states. So the equilibrium positions are in the minima of the corresponding potential energy surfaces. This decreases the influence of the electronic-vibronic interaction and, hence, the damping in the electronic subsystem. Finally, we should note that the damping rate in the population dynamics of the curve-crossing system cannot be increased to a very large value by increasing the system-bath coupling or the electronic-vibronic coupling.

5.4 Summary

In this chapter we derived the functional integral description of the population dynamics in the dissipative two-level system with vibrational sublevels. The damping rate of the coherent Rabi oscillations is obtained within the first order time-dependent perturbation theory in the squared coordinate shift between vibrational potential energy surfaces. We got simple analytical expressions for the damping rate in the high and low temperature regimes. The high temperature limit for the perturbative expansion for the complex frequency of the system is analyzed by the variational perturbation theory, and in this way we obtained the damping rate without the restriction to a small expansion parameter. More accurate results can be calculated by taking into account higher order perturbation terms. These terms must be evaluated using the vibronic generating functional with the non-linear interaction part. In other words, one has to be able to average the functionals of the form

$$\exp\left[\int_0^t ds_1 \int_0^t ds_2 \ldots \int_0^t ds_n \mathcal{R}(s_1, s_2, \ldots, s_n) r(s_1) \ldots r(s_k) q(s_{k+1}) \ldots q(s_n)\right] \qquad (5.78)$$

with the action of the damped harmonic oscillator in a perturbative manner and prevent the secular terms in the final result. Besides, the expansion of the whole result for the populations includes the expansions for the powers of the exponents as well as the expansions for the prefactors of those exponents. The implementation of the variational perturbation theory to such a form of the perturbation expansion consists of the optimization of a few separated expansions. This form of the optimization has not yet been derived but work in this direction is currently in progress.

Chapter 6

Conclusion

There are a lot of analytical and numerical treatments for the description of the dissipation in quantum systems and most of them are based on different forms of perturbation theories. For instance, solution of the master equations are usually restricted to the weak system-bath coupling while the evaluation of the corresponding path integrals often can be performed only if some of the parameters of the relevant system are small. Hence, different methods of calculation are valid in different ranges of the system parameters. In the present work we developed two perturbative analytic approaches for the single dissipative vibrational mode and for the dissipative curve-crossing dynamics.

First, we derived the real-time coherent-state path integral technique for the reduced density matrix. This approach has been tested for a quantum damped harmonic oscillator. Then the procedure of diagonalization of the Lagrangian leads to a very simple expression for the reduced dynamics in case of the rotating-wave approximation. The obtained result appears to be useful for the analysis of the population dynamics of the vibrational eigenstates while the standard phase-space path integral formulation with the influence functional approach is good for the description of the dynamics of the vibrational coordinate (e.g. evolution of the wave packets). The population dynamics is a quite important tool for the investigation of the decoherence in quantum systems. In order to study the influence of the initial preparation on the decoherence process we calculated the evolution of the population of the vibrational eigenstates in the presence and in the absence of initial correlation. It has been shown that in the former case one gets initial jolts in the population due to the fast decoherence at the beginning of the evolution while in the latter case those jolts disappear. We obtained classical trajectories for the relaxation of the system coordinate by taking into account the initial system-bath correlations.

Next, the important model of the dissipative two-level system with vibrational sublevels (curve-crossing system) has been investigated by the path integral method. We used the mapping approach which allows to formulate the discrete two-level system in terms of coherent-state path integrals while for the dissipative reaction coordinate the usual Feynman path integrals was used. After eliminating the bath one gets a non-Gaussian functional integral describing the reduced dynamics of the relevant system (electronic subsystem plus reaction coordinate). We evaluated this integral within the perturbation theory in case of weak coupling between electronic and vibrational subsystems. Physically this means a small coordinate shift between the potential energy surfaces for the vibrational mode. Thus, our results are valid for the small coordinate shift but not restricted to any other small parameters of the system. This range of the system parameters was not studied previously. The results for the vibrational dynamics obtained within present approach have been compared to the results of the Redfield theory in the low damping regime in order to investigate the validity range of our perturbative method. It turns out that one has good agreement at the beginning of the time evolution. But the deviation of the perturbation theory from the Redfield results increases approaching the thermal equilibrium due to the absence of the higher order expansion terms. We compared the short time evolution of the peak position of the Gaussian wave packet given by our method with the results of the Redfield theory with and without Markov approximation. It has been found that already at short times one observes memory effects in the evolution dynamics and these effects depend on the initial preparation of the vibrational subsystem. Since our treatment has not been restricted to factorized initial system-bath conditions, a possible extension of the method consists of calculating the influence of the initial system-bath correlation on the non-Markovian effects in the short-time vibrational dynamics. Additionally, we considered the overdamped regime. In this case the vibrational coordinate rapidly relaxes at the beginning of the evolution due to the direct influence of the bath and then slowly approaches its equilibrium position being driven by the electronic subsystem.

Finally, the time evolution of the population of the electronic states has been formulated in terms of path integrals within the perturbation theory in small electronic-vibrational coupling. In this case the standard perturbation expansion fails to work since it leads to the appearance of secular terms in the final result. In order to avoid this problem we constructed a modified form of the perturbation method expanding the solution for the stationary electronic trajectories in a small parameter. Using this treatment we obtained the leading term for the frequency of the coherent transitions between the electronic states. This term is responsible for damping of the coherent oscillations of the electronic population due to the coupling to the environment. We got analytic expressions for the damping rate at low and high temperatures of bath. The time and the temperature dependence of the obtained rate function in first order of the perturbation corresponds to that for the exactly solvable model of the unbiased dissipative two-level system without vibrational sublevels. We extended the validity range of our expansion to make it valid for large values of the coordinate shift in the case of high temperatures by applying the variational perturbation theory. The analysis of the result for large coordinate shift shows that the damping rate in the electronic subsystem decreases with increasing coordinate shift or system-bath coupling constant.

More precise results for the dissipative vibrational and population dynamics in the curve-crossing systems within present perturbative approach can be achieved by taking into account the terms of higher orders in the perturbative expansions. But the evaluation of those terms is connected to the calculation of the non-Gaussian functional integrals for the dissipative vibrational mode.

Actually, the form of the Hamiltonian of the electronic-vibrational coupling used in present work seems to be the most reasonable and general form of the interaction Hamiltonians in the models describing the dissipative quantum dynamics of complicated systems.

Thus, further development of the present perturbation theory (with the implementation of the variational perturbation theory) for the evaluation of the functional integrals can be important for the progress in the investigation of the time evolution of dissipative quantum systems. The methodology developed in this thesis presents the first step in this direction.

Appendix A

Diagonalization beyond rotating wave approximation

Here we will evaluate the path integral (3.10) with the Hamiltonian without RWA (3.34). First the renormalization term H_r will be neglected and reintroduced in the second part. The action (3.11) has the form

$$S(\{z_\omega(\tau)\},\{z_\omega^*(\tau)\}) = \frac{1}{2}\left[a^*(t)a(t) - a^*(0)a(0) + \sum_\omega z_\omega^*(t)z_\omega(t) - \sum_\omega z_\omega^*(0)z_\omega(0)\right] - \int_0^t \mathcal{L}(a(\tau),a^*(\tau),\{z_\omega^*(\tau)\},\{z_\omega(\tau)\})d\tau \tag{A.1}$$

where the Lagrangian $\mathcal{L}$ is given by

$$\begin{aligned}
&\mathcal{L}(a(\tau),a^*(\tau),\{z_\omega^*(\tau)\},\{z_\omega(\tau)\}) = \\
&\quad \frac{1}{2}\dot{a}(\tau)a^*(\tau) - \frac{1}{2}\dot{a}^*(\tau)a(\tau) + \frac{1}{2}\sum_\omega \dot{z}_\omega(\tau)z_\omega^*(\tau) - \frac{1}{2}\sum_\omega \dot{z}_\omega^*(\tau)z_\omega(\tau) \\
&\quad + i\omega_0 a^*(\tau)a(\tau) + i\sum_\omega \omega z_\omega^*(\tau)z_\omega(\tau) + i\sum_\omega k_\omega\{a^*(\tau)+a(\tau)\}\{z_\omega^*(\tau)+z_\omega(\tau)\}
\end{aligned} \tag{A.2}$$

which should be taken with the boundary conditions (3.39).

Going beyond the RWA we have to use an extended transformation, since the non-RWA terms in the interaction part of the Hamiltonian mix the operators a with a^+. The transformation which should be used in this case is

$$a = \sum_\Omega \alpha_\Omega A_\Omega + \sum_\Omega \tilde{\alpha}_\Omega A_\Omega^* \ , \tag{A.3}$$

$$a^* = \sum_\Omega \alpha_\Omega A_\Omega^* + \sum_\Omega \tilde{\alpha}_\Omega A_\Omega \ , \tag{A.4}$$

$$z_\omega = \sum_\Omega \beta_{\Omega\omega} A_\Omega + \sum_\Omega \tilde{\beta}_{\Omega\omega} A_\Omega^* \ , \tag{A.5}$$

$$z^*_\omega \;=\; \sum_\Omega \beta_{\Omega\omega} A^*_\Omega + \sum_\Omega \tilde{\beta}_{\Omega\omega} A_\Omega \; . \tag{A.6}$$

Below we will follow a similar procedure as within RWA. Substituting the trajectories $a, a^*, z_\omega, z^*_\omega$ as functions of A_Ω, A^*_Ω into the Lagrangian (A.2) we require the Lagrangian to have diagonal form after the transformation, i.e.

$$\begin{aligned}&\mathcal{L}(a(\tau), a^*(\tau), \{z^*_\omega(\tau)\}, \{z_\omega(\tau)\}) = \\ &\quad \frac{1}{2}\sum_\Omega \dot{A}_\Omega(\tau) A^*_\Omega(\tau) - \frac{1}{2}\sum_\Omega \dot{A}^*_\Omega(\tau) A_\Omega(\tau) + i\sum_\Omega \Omega A^*_\Omega(\tau) A_\Omega(\tau) \; .\end{aligned} \tag{A.7}$$

It leads to the following orthogonality relations for the transformation matrices

$$\alpha_\Omega \alpha_{\Omega'} - \tilde{\alpha}_\Omega \tilde{\alpha}_{\Omega'} + \sum_\omega \beta_{\Omega\omega}\beta_{\Omega'\omega} - \sum_\omega \tilde{\beta}_{\Omega\omega}\tilde{\beta}_{\Omega'\omega} \;=\; \delta_{\Omega\Omega'} \; , \tag{A.8}$$

$$\alpha_\Omega \tilde{\alpha}_{\Omega'} - \tilde{\alpha}_\Omega \alpha_{\Omega'} + \sum_\omega \beta_{\Omega\omega}\tilde{\beta}_{\Omega'\omega} - \sum_\omega \tilde{\beta}_{\Omega\omega}\beta_{\Omega'\omega} \;=\; 0 \tag{A.9}$$

and to the equations for the transformation matrix coefficients

$$\alpha_\Omega(\omega_0 - \Omega) \;=\; \tilde{\alpha}_\Omega(\omega_0 + \Omega) = -\sum_\omega k_\omega(\beta_{\Omega\omega} + \tilde{\beta}_{\Omega\omega}) \; , \tag{A.10}$$

$$\beta_{\Omega\omega}(\omega - \Omega) \;=\; \tilde{\beta}_{\Omega\omega}(\omega + \Omega) = -k_\omega(\alpha_\Omega + \tilde{\alpha}_\Omega) \; . \tag{A.11}$$

One may also diagonalize the Lagrangian including the renormalization (3.37). The renormalized Lagrangian $\mathcal{L}_R$ corresponding to the Hamiltonian (2.3) is the Lagrangian (A.2) with the additional term

$$\mathcal{L}_r = i\omega_R((a^*)^2 + a^2 + 2a^*a) \; , \tag{A.12}$$

with the renormalization frequency

$$\omega_R = \sum_\omega \frac{k^2_\omega}{\omega} \; . \tag{A.13}$$

It is obvious that the orthogonality relations (A.8) and (A.9) remain the same. Equation (A.10) for the transformation matrix coefficients changes and is now given by

$$\alpha_\Omega(\omega_0 - \Omega) = \tilde{\alpha}_\Omega(\omega_0 + \Omega) = -\sum_\omega k_\omega(\beta_{\Omega\omega} + \tilde{\beta}_{\Omega\omega}) - 2\omega_R(\alpha_\Omega + \tilde{\alpha}_\Omega) \; . \tag{A.14}$$

Eq. (A.11) remains the same.

The back transformation reads

$$A_\Omega \;=\; \alpha_\Omega a - \tilde{\alpha}_\Omega a^* + \sum_\omega \beta_{\Omega\omega} z_\omega - \sum_\omega \tilde{\beta}_{\Omega\omega} z^*_\omega \; , \tag{A.15}$$

$$A^*_\Omega \;=\; \alpha_\Omega a^* - \tilde{\alpha}_\Omega a + \sum_\omega \beta_{\Omega\omega} z^*_\omega - \sum_\omega \tilde{\beta}_{\Omega\omega} z_\omega \; . \tag{A.16}$$

The final step is to find the additional orthogonality relations for the transformation matrices. Substituting A_Ω and A^*_Ω as functions of $a, a^*, z_\omega, z^*_\omega$ (A.15, A.16) into Eq. (A.3-A.6) and using the orthogonality of the transformation one obtains

$$\begin{aligned}
\sum_\Omega (\alpha_\Omega^2 - \tilde{\alpha}_\Omega^2) &= 1 \;, && \text{(A.17)}\\
\sum_\Omega (\alpha_\Omega \beta_{\Omega\omega} - \tilde{\alpha}_\Omega \tilde{\beta}_{\Omega\omega}) &= 0 \;, && \text{(A.18)}\\
\sum_\Omega (\alpha_\Omega \tilde{\beta}_{\Omega\omega} - \tilde{\alpha}_\Omega \beta_{\Omega\omega}) &= 0 \;, && \text{(A.19)}\\
\sum_\Omega (\beta_{\Omega\omega} \beta_{\Omega\omega'} - \tilde{\beta}_{\Omega\omega} \tilde{\beta}_{\Omega\omega'}) &= \delta_{\omega\omega'} \;, && \text{(A.20)}\\
\sum_\Omega (\beta_{\Omega\omega} \tilde{\beta}_{\Omega\omega'} - \tilde{\beta}_{\Omega\omega} \beta_{\Omega\omega'}) &= 0 \;. && \text{(A.21)}
\end{aligned}$$

The Lagrangian (A.7) describes a system of independent harmonic oscillators. Applying the stationary-phase method we get the stationary trajectories (3.54) and the Lagrangian is equal to zero at the stationary point.

For the matrix element of the evolution operator one gets

$$\begin{aligned}
\langle \{z_\omega\} | \langle a | e^{-iHt} | a' \rangle | \{z'_\omega\} \rangle = \exp\Bigg[&-\frac{1}{2}|a|^2 - \frac{1}{2}|a'|^2 - \frac{1}{2}\sum_\omega |z_\omega|^2 - \frac{1}{2}\sum_\omega |z'_\omega|^2 \\
&+ \frac{1}{2}\left(a^*(t)a(t) - a^*(0)a(0) + \sum_\omega z^*_\omega(t) z_\omega(t) - \sum_\omega z^*_\omega(0) z_\omega(0) \right) \Bigg] \;. \qquad \text{(A.22)}
\end{aligned}$$

Using the boundary conditions (3.39) and the solution for the stationary trajectories (3.54) we find the connection between the end points of the trajectories $a(\tau), a^*(\tau), z_\omega(\tau), z^*_\omega(\tau)$ at times $\tau = 0$ and $\tau = t$

$$a(0) = \Lambda(t)a(t) + \tilde{\Lambda}(t)a^*(t) + \sum_\omega \Delta_\omega(t) z_\omega(t) + \sum_\omega \tilde{\Delta}_\omega(t) z^*_\omega(t) \;, \qquad \text{(A.23)}$$

$$z_\omega(0) = \Delta_\omega(t)a(t) - \tilde{\Delta}^*_\omega(t)a^*(t) + \sum_{\omega'} \Gamma_{\omega\omega'}(t) z_{\omega'}(t) + \sum_{\omega'} \tilde{\Gamma}_{\omega\omega'}(t) z^*_{\omega'}(t) \;, \qquad \text{(A.24)}$$

$$a^*(0) = \Lambda^*(t)a^*(t) + \tilde{\Lambda}^*(t)a(t) + \sum_\omega \Delta^*_\omega(t) z^*_\omega(t) + \sum_\omega \tilde{\Delta}^*_\omega(t) z_\omega(t) \;, \qquad \text{(A.25)}$$

$$z^*_\omega(0) = \Delta^*_\omega(t)a^*(t) - \tilde{\Delta}_\omega(t)a(t) + \sum_{\omega'} \Gamma^*_{\omega\omega'}(t) z^*_{\omega'}(t) + \sum_{\omega'} \tilde{\Gamma}^*_{\omega\omega'}(t) z_{\omega'}(t) \;, \qquad \text{(A.26)}$$

where

$$\Lambda(t) = \sum_\Omega (\alpha_\Omega^2 e^{i\Omega t} - \tilde{\alpha}_\Omega^2 e^{-i\Omega t}) \;, \qquad \text{(A.27)}$$

$$\tilde{\Lambda}(t) = \sum_{\Omega}(\tilde{\alpha}_{\Omega}\alpha_{\Omega}e^{-i\Omega t} - \alpha_{\Omega}\tilde{\alpha}_{\Omega}e^{i\Omega t}) \ , \tag{A.28}$$

$$\Delta_{\omega}(t) = \sum_{\Omega}(\alpha_{\Omega}\beta_{\Omega\omega}e^{-i\Omega t} - \tilde{\alpha}_{\Omega}\tilde{\beta}_{\Omega\omega}e^{i\Omega t}) \ , \tag{A.29}$$

$$\tilde{\Delta}_{\omega}(t) = \sum_{\Omega}(\tilde{\alpha}_{\Omega}\beta_{\Omega\omega}e^{-i\Omega t} - \alpha_{\Omega}\tilde{\beta}_{\Omega\omega}e^{i\Omega t}) \ , \tag{A.30}$$

$$\Gamma_{\omega\omega'}(t) = \sum_{\Omega}(\beta_{\Omega\omega}\beta_{\Omega\omega'}e^{i\Omega t} - \tilde{\beta}_{\Omega\omega}\tilde{\beta}_{\Omega\omega'}e^{-i\Omega t}) \ , \tag{A.31}$$

$$\tilde{\Gamma}_{\omega\omega'}(t) = \sum_{\Omega}(\tilde{\beta}_{\Omega\omega}\beta_{\Omega\omega'}e^{-i\Omega t} - \beta_{\Omega\omega}\tilde{\beta}_{\Omega\omega'}e^{i\Omega t}) \ . \tag{A.32}$$

The expression (A.22) for the matrix element of the evolution operator depending on the end points of the trajectories together with Eqs. (A.23-A.32) will be used for the calculation of the population dynamics in subsection 3.2.5.

Appendix B

Reduced density matrix within rotating wave approximation

In this appendix we will give the details of the procedure for calculating the result (3.81). First, using the result (3.58) and the initial conditions (3.78,3.79) we can write the time evolution of the reduced density matrix of the system oscillator in the following form

$$\langle a|\rho_s(t)|a'\rangle = \int \frac{da_1 da_1^*}{\pi}\frac{da_2 da_2^*}{\pi}\prod_\omega \frac{dz_\omega dz_\omega^*}{\pi}\frac{dz_{1\omega} dz_{1\omega}^*}{\pi}\frac{dz_{2\omega} dz_{2\omega}^*}{\pi}$$
$$\times \exp\Bigg[-\frac{|a|^2}{2}-\frac{|a'|^2}{2}-|a_1|^2-|a_2|^2-\sum_\omega\Big(|z_\omega|^2-|z_{1\omega}|^2-|z_{2\omega}|^2\Big)$$
$$+\xi(t)a^*a_1+\sum_\omega \eta_\omega(t)(a^*z_{1\omega}+a_1 z_\omega^*)+\sum_{\omega,\omega'}\mu_{\omega,\omega'}(t)z_\omega^* z_{1\omega'}+f_0(a_1^*,a_2)$$
$$+\xi^*(t)a_2^*a'+\sum_\omega \eta_\omega^*(t)(a_2^* z_\omega+a' z_{2\omega}^*)+\sum_{\omega,\omega'}\mu_{\omega,\omega'}^*(t)z_{2\omega}^* z_{\omega'}+\sum_\omega e^{-\omega/T_b} z_{1\omega}^* z_{2\omega}\Bigg] . \tag{B.1}$$

Tracing out the bath, i.e. integrating over the end points of bath trajectories z_ω, and using the orthogonality relations (3.51-3.53) and the expressions for the coefficients ξ, η, μ Eq. (3.59-3.61), one gets

$$\langle a|\rho_s(t)|a'\rangle = \int \frac{da_1 da_1^*}{\pi}\frac{da_2 da_2^*}{\pi}\exp\Bigg[-\frac{|a|^2}{2}-\frac{|a'|^2}{2}-|a_1|^2-|a_2|^2$$
$$+\xi(t)a^*a_1+\xi^*(t)a_2^*a'+f_0(a_1^*,a_2)+(1-|\xi(t)|^2)a_1a_2^*\Bigg]$$
$$\times\int\prod_\omega \frac{dz_{1\omega} dz_{1\omega}^*}{\pi}\frac{dz_{2\omega} dz_{2\omega}^*}{\pi}\exp\Big[-\sum_\omega\Big(|z_{1\omega}|^2+|z_{2\omega}|^2\Big)+\mathcal{F}\Big] , \tag{B.2}$$

where the function $\mathcal{F}$ is determined as

$$\mathcal{F} = \sum_\omega\Big[e^{-\omega/T_b} z_{1_\omega}^* z_{2\omega}+z_{1_\omega} z_{2\omega}^*+\sum_{\omega'}\eta_\omega(t)\eta_{\omega'}^*(t)z_{1\omega}z_{2\omega'}^*$$
$$+z_{1\omega}\eta_\omega(t)(a^*-\xi^*(t)a_2^*)+z_{2\omega}^*\eta_\omega^*(t)(a'-\xi(t)a_1)\Big] . \tag{B.3}$$

Then, one can separate the integrals over the system and bath end points introducing new integration variables $\delta z_{n\omega}$ and $\delta z^*_{n\omega}$ $(n = 1, 2)$ as

$$z_{n\omega} = \bar{z}_{n\omega} + \delta z_{n\omega} \ , \qquad z^*_{n\omega} = \bar{z}^*_{n\omega} + \delta z^*_{n\omega} \ . \tag{B.4}$$

The fixed points $\bar{z}_{n\omega}$ and $\bar{z}^*_{n\omega}$ depend on the system end points and can be obtained from the condition

$$\frac{\partial \mathcal{F}}{\partial z_{n\omega}} = 0 \ , \qquad \frac{\partial \mathcal{F}}{\partial z^*_{n\omega}} = 0. \tag{B.5}$$

The solution of the system (B.5) reads

$$\begin{aligned} &\bar{z}^*_{2\omega} = \bar{z}^*_{1\omega} e^{-\omega/T_b} \ , \qquad \bar{z}_{2\omega} = \bar{z}_{1\omega} e^{-\omega/T_b} \ , \\ &\bar{z}_{1\omega} = \frac{n_\omega \eta^*_\omega(t)}{1+Q}(a' - \xi(t) a_1) \ , \qquad \bar{z}^*_{2\omega} = \frac{n_\omega \eta_\omega(t)}{1+Q}(a^* - \xi^*(t) a^*_2) \ , \end{aligned} \tag{B.6}$$

where the functions Q and n_ω are given by Eq. (3.82). Finally, substituting the replacement (B.4) into the integral (B.2) and taking into account Eqs. (B.6) one gets the result (3.81) where the unknown function F is the integral over the deviations $\delta z_{n\omega}$ and $\delta z^*_{n\omega}$

$$\begin{aligned} F \ = \ & \int \prod_\omega \frac{d\delta z_{1\omega} d\delta z^*_{1\omega}}{\pi} \frac{d\delta z_{2\omega} d\delta z^*_{2\omega}}{\pi} \exp\Big[\sum_\omega \Big(-|\delta z_{1\omega}|^2 - |\delta z_{2\omega}|^2 \\ & + e^{-\omega/T_b} \delta z^*_{1_\omega} \delta z_{2\omega} + \delta z_{1_\omega} \delta z^*_{2\omega} + \sum_{\omega'} \eta_\omega(t) \eta^*_{\omega'}(t) \delta z_{1\omega} \delta z^*_{2\omega'} \Big) \Big] \ . \end{aligned} \tag{B.7}$$

Appendix C

Evolution of the reduced density matrix with initial correlations

The purpose is to calculate the matrix element of the reduced density matrix

$$\frac{1}{Z_{sb}}\langle a|e^{-iHt}e^{-\lambda\tilde{H}}e^{iHt}|a'\rangle \tag{C.1}$$

with $Z_{sb} = \text{Tr}\ e^{-\lambda\tilde{H}}$ and λ being the inverse temperature. Writing the matrix element of the initial density operator $e^{-\lambda\tilde{H}}$ as an imaginary-time path integral and using the procedure of diagonalization of the Lagrangian presented in subsection 3.2.2, one gets

$$\begin{aligned}\langle z_\omega|\langle a|e^{-\lambda\tilde{H}}|a'\rangle|z'_\omega\rangle = \exp\Big[&-\frac{|a|^2}{2} - \frac{|a'|^2}{2} - \sum_\omega \frac{|z_\omega|^2}{2} - \sum_\omega \frac{|z'_\omega|^2}{2} \\ &+a^*a'\tilde{\xi}(\lambda) + \sum_\omega \tilde{\eta}(\lambda)(a^*z'_\omega + a'z^*_\omega) + \sum_{\omega\omega'} \tilde{\mu}_{\omega\omega'}(\lambda) z^*_\omega z'_{\omega'} \\ -\varphi_1(\lambda)a^* - \varphi_2(\lambda)a' &- \sum_\omega \chi_{1\omega}(\lambda) z^*_\omega - \sum_\omega \chi_{2\omega}(\lambda) z'_\omega + \chi_0(\lambda)\Big]\ ,\end{aligned} \tag{C.2}$$

where

$$\begin{aligned}\tilde{\xi}(\lambda) &= \sum_\Omega \alpha_\Omega^2 e^{-\Omega\lambda}\ , & \text{(C.3)}\\ \tilde{\eta}_\omega(\lambda) &= \sum_\Omega \alpha_\Omega \beta_{\Omega\omega} e^{-\Omega\lambda}\ , & \text{(C.4)}\\ \tilde{\mu}_{\omega\omega'}(\lambda) &= \sum_\Omega \beta_{\Omega\omega}\beta_{\Omega\omega'} e^{-\Omega\lambda}\ , & \text{(C.5)}\end{aligned}$$

$$\varphi_1(\lambda) = q\sum_\Omega \alpha_\Omega^2 \int_0^\lambda e^{-\Omega(\lambda-s)} ds\ , \tag{C.6}$$

$$\varphi_2(\lambda) = q\sum_\Omega \alpha_\Omega^2 \int_0^\lambda e^{-\Omega s} ds\ , \tag{C.7}$$

$$\chi_{1\omega}(\lambda) \;=\; q\sum_{\Omega}\alpha_{\Omega}\beta_{\Omega\omega}\int_0^{\lambda} e^{-\Omega(\lambda-s)}ds \;, \tag{C.8}$$

$$\chi_{2\omega}(\lambda) \;=\; q\sum_{\Omega}\alpha_{\Omega}\beta_{\Omega\omega}\int_0^{\lambda} e^{-\Omega s}ds \;, \tag{C.9}$$

$$\chi_{0}(\lambda) \;=\; q^2\sum_{\Omega}\alpha_{\Omega}^2\int_0^{\lambda}\int_0^{s} e^{-\Omega(s-s')}ds'ds \;. \tag{C.10}$$

Below we will consider the case $T=0$ $(\lambda=\infty)$. Hence $\tilde{\xi}(\lambda)=\tilde{\eta}_{\omega}(\lambda)=\tilde{\mu}_{\omega\omega'}(\lambda)=0$. Then, using Eq. (C.2) together with our result for the matrix element of the evolution operator (3.58) and integrating over the end points of the trajectories one obtains for the matrix element (C.1)

$$\begin{aligned}
\langle a|e^{-iHt}e^{-\lambda\tilde{H}}e^{iHt}|a'\rangle &= \tilde{F}(t)\exp\Big[-\frac{|a|^2}{2}-\frac{|a'|^2}{2}-\varepsilon_1(t)a^*-\varepsilon_2(t)a'\Big]\;, && \text{(C.11)}\\
\varepsilon_1(t) &= \xi(t)\varphi_1+\sum_{\omega}\eta_{\omega}(t)\chi_{1\omega}\;, && \text{(C.12)}\\
\varepsilon_2(t) &= \xi^*(t)\varphi_2+\sum_{\omega}\eta^*_{\omega}(t)\chi_{2\omega}\;, && \text{(C.13)}
\end{aligned}$$

where the pre-exponential factor $\tilde{F}(t)$ is an unknown function of time coming from the integration over the end points of the bath trajectories. Using the normalization condition Tr $\rho(t)=1$ one obtains

$$\tilde{F}(t)=e^{-\varepsilon_1(t)\varepsilon_2(t)}\;. \tag{C.14}$$

Finally, using Eqs. (C.6-C.9) for zero temperature $(\lambda=\infty)$ and introducing $\varepsilon=\varepsilon_1(\lambda=\infty)$ and $\varepsilon^*=\varepsilon_2(\lambda=\infty)$ one gets the result (3.103).

Appendix D

Calculation of the generating functional for the electronic subsystem

First, let us calculate the functional integral of the form

$$\begin{aligned} W[j(\tau), j^*(\tau)] &= \int D[a_1(\tau), a_1^*(\tau)] D[a_2(\tau), a_2^*(\tau)] \\ &\times \exp\left(-\frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2} + S'_{el}[\{a_n\}, \{a_n^*\}]\right) \end{aligned} \quad ,\text{(D.1)}$$

where the action S'_{el} is determined by Eq. (4.55). After the integration using the stationary-phase method with the boundary conditions (4.15) for the trajectories $a_n(\tau)$ and $a_n^*(\tau)$ the result W is the functional of the auxiliary sources j and j^* and reads

$$W[j(\tau), j^*(\tau)] = \exp\left(-\frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2} + \bar{S}'_{el}\right) . \tag{D.2}$$

Here $\bar{S}'_{el}$ is the electronic action $S'_{el}[\{a_n\}, \{a_n^*\}]$ taken on the stationary trajectories

$$\begin{aligned} \bar{S}'_{el} &= a_1^* a_1' \xi_{11}(t) + a_2^* a_2' \xi_{22}(t) + a_1' a_2^* \xi_{12}(t) + a_2' a_1^* \xi_{21}(t) \\ &+ a_1^* \bar{J}_1[j^*(\tau)] + a_1' J_1[j(\tau)] + a_2^* \bar{J}_2[j^*(\tau)] + a_2' J_2[j(\tau)] + \Gamma[j(\tau), j^*(\tau')] , \end{aligned} \tag{D.3}$$

where

$$\begin{aligned} \xi_{11}(\tau) &= \sin^2\varphi e^{-i\Omega_1\tau} + \cos^2\varphi e^{-i\Omega_2\tau} , \\ \xi_{22}(\tau) &= \cos^2\varphi e^{-i\Omega_1\tau} + \sin^2\varphi e^{-i\Omega_2\tau} , \\ \xi_{12}(\tau) &= \xi_{21}(\tau) = \sin\varphi\cos\varphi\left(e^{-i\Omega_1\tau} - e^{-i\Omega_2\tau}\right) , \end{aligned} \tag{D.4}$$

$$J_1[j(\tau)] = \int_0^t d\tau j(\tau)\xi_{12}(\tau) , \qquad \bar{J}_1[j(\tau)] = \int_0^t d\tau j(\tau)\xi_{12}(t-\tau) , \tag{D.5}$$

$$J_2[j(\tau)] = \int_0^t d\tau j(\tau)\xi_{22}(\tau) \;, \qquad \bar{J}_2[j(\tau)] = \int_0^t d\tau j(\tau)\xi_{22}(t-\tau) \;, \tag{D.6}$$

$$\Gamma[j(\tau), j^*(\tau')] = \int_0^t d\tau \int_0^\tau d\tau' j(\tau) j^*(\tau')\xi_{22}(\tau-\tau') \;. \tag{D.7}$$

The frequencies $\Omega_{1,2}$ and the angle φ are defined in Eqs. (4.58-4.60). This functional corresponds to the forward path integral, i.e. the matrix element of the evolution operator $e^{-iH_{el}t}$ with the Hamiltonian $H_{el} = \epsilon a_2^+ a_2 + \Delta(a_1^+ a_2 + a_2^+ a_1)$ of the pure electronic subsystem. Analogously, the functional corresponding to the backward path integral is given by

$$\begin{aligned} \tilde{W}[\tilde{j}(\tau), \tilde{j}^*(\tau)] &= \int D[\tilde{a}_1(\tau), \tilde{a}_1^*(\tau)] D[\tilde{a}_2(\tau), \tilde{a}_2^*(\tau)] \\ &\quad \times \exp\left(-\frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2} + \tilde{S}_{el}'[\{\tilde{a}_n\}, \{\tilde{a}_n^*\}] \right) \\ &= \exp\left(-\frac{|a_1|^2}{2} - \frac{|a_2|^2}{2} - \frac{|a_1'|^2}{2} - \frac{|a_2'|^2}{2} + \bar{\tilde{S}}_{el}' \right) \;, \end{aligned} \tag{D.8}$$

where the boundary conditions (4.18) were used and the action $\bar{\tilde{S}}_{el}'$ evaluated on the stationary trajectories reads

$$\begin{aligned} \bar{\tilde{S}}_{el}' &= a_1^* a_1' \xi_{11}^*(t) + a_2^* a_2' \xi_{22}^*(t) + a_1' a_2^* \xi_{12}^*(t) + a_2' a_1^* \xi_{21}^*(t) \\ &\quad + a_1^* J_1^*[\tilde{j}^*(\tau)] + a_1' \bar{J}_1^*[\tilde{j}(\tau)] + a_2^* J_2^*[\tilde{j}^*(\tau)] + a_2' \bar{J}_2^*[\tilde{j}(\tau)] + \Gamma^*[\tilde{j}^*(\tau), \tilde{j}(\tau')] \;. \end{aligned} \tag{D.9}$$

Next, we can compose the functional for the full density matrix of the electronic subsystem using the functionals for the forward and backward path integrals (D.1) and (D.8) and initial condition (4.19). Integrating over the end points of the trajectories, one gets the generating functionals corresponding to the populations of the first (Ξ_1) and second (Ξ_2) electronic state

$$\begin{aligned} \Xi_1[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)] &= \Big(\xi_{11}(t) + J_1[j(\tau)]\bar{J}_1[j^*(\tau)]\Big)\Big(\xi_{11}^*(t) + \bar{J}_1^*[\tilde{j}(\tau)] J_1^*[\tilde{j}^*(\tau)]\Big) \\ &\quad \times \exp\Big(\Gamma[j(\tau), j^*(\tau)] + \Gamma^*[\tilde{j}(\tau), \tilde{j}^*(\tau)]\Big) \;, \\ \Xi_2[j(\tau), j^*(\tau), \tilde{j}(\tau), \tilde{j}^*(\tau)] &= \Big(\xi_{12}(t) + J_1[j(\tau)]\bar{J}_2[j^*(\tau)]\Big)\Big(\xi_{12}^*(t) + J_1^*[\tilde{j}^*(\tau)]\bar{J}_2^*[\tilde{j}(\tau)]\Big) \\ &\quad \times \exp\Big(\Gamma[j(\tau), j^*(\tau)] + \Gamma^*[\tilde{j}(\tau), \tilde{j}^*(\tau)]\Big) \;. \end{aligned} \tag{D.10}$$

Finally, in order to get the trace over the electronic states one has to calculate the sum $\Xi = \Xi_1 + \Xi_2$. This leads to the result (4.57).

Appendix E

Calculation of the Green's function

Here we will calculate the Green's function (4.39) in case of Ohmic dissipation (3.75). Using expression (4.28) for the damping kernel $\gamma(s)$ one finds its Laplace transform

$$\hat{\gamma}(p) = \sum_{\omega} \frac{c_{\omega}^2}{M m_{\omega} \omega} \frac{\omega}{p^2 + \omega^2} \ . \tag{E.1}$$

The inverse Laplace transform for the Greens function $G(s)$ reads

$$G(s) = \lim_{\sigma_1 \to \infty} \frac{1}{2\pi i} \int_{-i\sigma_1 + \sigma_2}^{i\sigma_1 + \sigma_2} dp \frac{e^{ps}}{p^2 + \tilde{\omega}^2 - \hat{\gamma}(p)} \ . \tag{E.2}$$

Then, substituting Eq. (E.1) into Eq. (E.2), using the relation (3.35) and replacing the integrational variable p in the integral in Eq. (E.2) by $-i\Omega$, for the Green's function one gets

$$G(s) = \lim_{\sigma_1 \to \infty} \frac{1}{2\pi i} \int_{-\sigma_1 + i\sigma_2}^{\sigma_1 + i\sigma_2} d\Omega \frac{e^{-i\Omega s}}{\Omega^2 - \tilde{\omega}^2 - 4\omega_0 \sum_{\omega} \frac{\omega k_{\omega}^2}{\Omega^2 - \omega^2}} \ . \tag{E.3}$$

Now one can see that the denominator of the integrand on the right hand side of Eq. (E.3) represents the spectral equation without the RWA Eq. (3.66) which has the solution (3.77) in case of Ohmic dissipation. The evaluation of the integral (E.3) leads to the result (4.72).

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Erklärung gemäß Promotionsordnung §6 (2) 4, 5

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe. Die Stellen in der Arbeit, die in Sinn und Wortlaut anderen Werken entnommen wurden, habe ich entsprechend gekennzeichnet. Ich erkläre, nicht bereits früher oder gleichzeitig bei anderen Hochschulen oder an der Universität Chemnitz ein Promotionsverfahren beantragt zu haben. Die derzeit gültige Promotionsordnung der Fakultät für Naturwissenschaften der Technischen Universität Chemnitz vom 10. Oktober 2001 ist mir bekannt.

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